



ANNUAL REPORTS  
ON THE  
PROGRESS OF CHEMISTRY.





# ANNUAL REPORTS

ON THE

## PROGRESS OF CHEMISTRY

### FOR 1908.

ISSUED BY THE CHEMICAL SOCIETY.

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#### Contributors:

C. H. DESCH, D.Sc., Ph.D.	A. R. LING, F.I.C.
A. FINDLAY, M.A., D.Sc., Ph.D.	H. MARSHALL, D.Sc., F.R.S.
A. D. HALL, M.A.	G. T. MORGAN, D.Sc.
W. D. HALLIBURTON, M.D., F.R.S.	W. J. POPE, M.A., M.Sc., F.R.S.

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## CONTENTS.

	PAGE
GENERAL AND PHYSICAL CHEMISTRY. By ALEXANDER FINDLAY, M.A., D.Sc., Ph.D. . . . .	1
INORGANIC CHEMISTRY. By HUGH MARSHALL, D.Sc., F.R.S. . . .	31
ORGANIC CHEMISTRY. By CECIL H. DESCH, D.Sc., Ph.D., and GILBERT T. MORGAN, D.Sc. . . . .	73
ANALYTICAL CHEMISTRY. By ARTHUR ROBERT LING, F.I.C. . . .	180
PHYSIOLOGICAL CHEMISTRY. By W. D. HALLIBURTON, M.D., F.R.S.	210
AGRICULTURAL CHEMISTRY AND VEGETABLE PHYSIOLOGY. By A. D. HALL, M.A. . . . .	242
CRYSTALLOGRAPHY. By WILLIAM JACKSON POPE, M.A., M.Sc., F.R.S.	258

#### ERRATUM.

IN last year's Report on Analytical Chemistry (*Ann. Report*, 1907, 215), in referring to an investigation by Cochran, the writer overlooked the fact that the effect of acid mercuric nitrate solution on the polarisation of lactose had already been studied by J. B. P. Harrison (*Analyst*, 1904, 29, 253), who had arrived at precisely the same conclusion.

# TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
<i>A.</i> . . . . .	Abstracts in Journal of the Chemical Society.*
<i>Amer. Chem. J.</i> . . . . .	American Chemical Journal.
<i>Amer. J. Physiol.</i> . . . . .	American Journal of Physiology.
<i>Amer. J. Sci.</i> . . . . .	American Journal of Science.
<i>Analyst</i> . . . . .	The Analyst.
<i>Annalen</i> . . . . .	Justus Liebig's Annalen der Chemie.
<i>Ann. Chim. anal.</i> . . . . .	Annales de Chimie analytique appliquée à l'Industrie. à l'Agriculture, à la Pharmacie et à la Biologie.
<i>Ann. Chim. Phys.</i> . . . . .	Annales de Chimie et de Physique.
<i>Ann. of Botany.</i> . . . . .	Annals of Botany.
<i>Ann. Report</i> . . . . .	Annual Reports of the Chemical Society.
<i>Apoth. Zeit.</i> . . . . .	Apotheker Zeitung.
<i>Arch. exp. Path. Pharm.</i> . . . . .	Archiv. für experimentelle Pathologie und Pharmakologie.
<i>Arch. Hygiene</i> . . . . .	Archiv für Hygiene.
<i>Arch. Pharm.</i> . . . . .	Archiv der Pharmazie.
<i>Atti R. Accad. Sci. Torino.</i> . . . . .	Atti della Reale Accademia delle Scienze di Torino.
<i>Atti R. Accad. Lincei</i> . . . . .	Atti della Reale Accademia dei Lincei.
<i>Beitr. chem. Physiol. Path.</i> . . . . .	Beiträge für chemische Physiologie und Pathologie.
<i>Ber.</i> . . . . .	Berichte der Deutschen chemischen Gesellschaft.
<i>Ber. Deut. bot. Ges.</i> . . . . .	Berichte der Deutschen botanischen Gesellschaft.
<i>Bied. Zentr.</i> . . . . .	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb
<i>Biochem. Zeitsch.</i> . . . . .	Biochemische Zeitschrift.
<i>Boll. chim. farm.</i> . . . . .	Bollettino chimico farmaceutico.
<i>Bull. Acad. Sci. Cracov</i> . . . . .	Bulletin international de l'Académie des Sciences de Cracovie.
<i>Bull. Coll. Agr. Tōkyō</i> . . . . .	Bulletin of the College of Agriculture, Imperial University, Tōkyō.
<i>Bull. Soc. chim.</i> . . . . .	Bulletin de la Société chimique de France.
<i>Bull. Soc. chim. Belg.</i> . . . . .	Bulletin de la Société chimique de Belgique.
<i>Bull. Soc. franç. Min.</i> . . . . .	Bulletin de la Société française de Minéralogie.
<i>Centr. Bakt. Par.</i> . . . . .	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
<i>Centr. Min.</i> . . . . .	Centralblatt für Mineralogie, Geologie und Palaeontologie.
<i>Chem. Zentr.</i> . . . . .	Chemisches Zentralblatt.
<i>Chem. News</i> . . . . .	Chemical News.
<i>Chem. Rev. Fett-Harz-Ind.</i> . . . . .	Chemische Revue über die Fett- und Harz-Industrie
<i>Chem. Weekblad</i> . . . . .	Chemische Weekblad.
<i>Chem. Zeit.</i> . . . . .	Chemiker Zeitung.
<i>Compt. rend.</i> . . . . .	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
<i>Gazzetta</i> . . . . .	Gazzetta chimica italiana.
<i>J. Agric. Sci.</i> . . . . .	Journal of Agricultural Science.
<i>J. Amer. Chem. Soc.</i> . . . . .	Journal of the American Chemical Society.
<i>J. Biol. Chem.</i> . . . . .	Journal of Biological Chemistry, New York.
<i>J. Chim. phys.</i> . . . . .	Journal de Chimie physique.
<i>J. Inst. Brewing.</i> . . . . .	Journal of the Institute of Brewing.
<i>J. Path. Bact.</i> . . . . .	Journal of Pathology and Bacteriology.

\* The year is not inserted in references to 1908.

viii TABLE OF ABBREVIATIONS EMPLOYED IN THE REFERENCES.

ABBREVIATED TITLE.	JOURNAL.
<i>J. Pharm. Chem.</i> . . .	Journal de Pharmacie et de Chimie.
<i>J. Physical Chem.</i> . . .	Journal of Physical Chemistry.
<i>J. Physiol.</i> . . .	Journal of Physiology.
<i>J. pr. Chem.</i> . . .	Journal für praktische Chemie.
<i>J. Russ. Phys. Chem. Soc.</i> . . .	Journal of the Physical and Chemical Society of Russia.
<i>J. Soc. Chem. Ind.</i> . . .	Journal of the Society of Chemical Industry.
<i>Landw. Versuchs-Stat.</i> . . .	Die landwirtschaftlichen Versuchs-Stationen.
<i>Mem. Manchester Phil. Soc.</i>	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
<i>Metallurgie</i> . . .	Metallurgie.
<i>Min. Mag.</i> . . .	Mineralogical Magazine and Journal of the Mineralogical Society.
<i>Monatsh.</i> . . .	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
<i>Mon. Sci.</i> . . .	Moniteur scientifique.
<i>Pflüger's Archiv</i> . . .	Archiv für die gesammte Physiologie des Menschen und der Thiere.
<i>Pharm. J.</i> . . .	Pharmaceutical Journal.
<i>Pharm. Rev.</i> . . .	Pharmaceutical Review.
<i>Pharm. Weekblad</i> . . .	Pharmaceutisch Weekblad.
<i>Pharm. Zeit.</i> . . .	Pharmazeutische Zeitung.
<i>Pharm. Zentr.-h.</i> . . .	Pharmazeutische Zentrallhalle.
<i>Phil. Mag.</i> . . .	Philosophical Magazine (The London, Edinburgh and Dublin).
<i>Phil. Trans.</i> . . .	Philosophical Transactions of the Royal Society of London.
<i>Physikal. Zeitsch.</i> . . .	Physikalische Zeitschrift.
<i>Proc.</i> . . .	Proceedings of the Chemical Society.
<i>Proc. Camb. Phil. Soc.</i> . . .	Proceedings of the Cambridge Philosophical Society.
<i>Proc. K. Akad. Wetensch. Amsterdam.</i>	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
<i>Proc. Physiol. Soc.</i> . . .	Proceedings of the Physiological Society.
<i>Proc. Roy. Soc.</i> . . .	Proceedings of the Royal Society.
<i>Quart. J. exp. Physiol.</i> . . .	Quarterly Journal of experimental Physiology.
<i>Rec. trav. chim.</i> . . .	Receuil des travaux chimiques des Pays-Bas et de la Belgique.
<i>Rev. intern. Falsif.</i> . . .	Revue internationale des Falsifications.
<i>Sci. Proc. Roy. Dubl. Soc.</i> . . .	Scientific Proceedings of the Royal Dublin Society.
<i>Sitzungsber. K. Akad. Wiss. Berlin.</i>	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
<i>Tech. Quart.</i> . . .	Technology Quarterly.
<i>Trans.</i> . . .	Transactions of the Chemical Society.
<i>Trans. Faraday Soc.</i> . . .	Transactions of the Faraday Society.
<i>Trans. Roy. Soc. Edin.</i> . . .	Transactions of the Royal Society of Edinburgh.
<i>Zeitsch. anal. Chem.</i> . . .	Zeitschrift für analytische Chemie.
<i>Zeitsch. angew. Chem.</i> . . .	Zeitschrift für angewandte Chemie.
<i>Zeitsch. anorg. Chem.</i> . . .	Zeitschrift für anorganische Chemie.
<i>Zeitsch. Chem. Ind. Kolloide.</i>	Zeitschrift für Chemie und Industrie der Kolloide.
<i>Zeitsch. Elektrochem.</i> . . .	Zeitschrift für Elektrochemie.
<i>Zeitsch. Kryst. Min.</i> . . .	Zeitschrift für Krystallographie und Mineralogie.
<i>Zeitsch. Nahr. Genussm.</i> . . .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
<i>Zeitsch. öffentl. Chem.</i> . . .	Zeitschrift für öffentliche Chemie.
<i>Zeitsch. physikal. Chem.</i> . . .	Zeitschrift für physikalische Chemie Stochiometrie und Verwandtschaftslehre.
<i>Zeitsch. physiol. Chem.</i> . . .	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
<i>Zeitsch. Ver. deut. Zuckerind.</i>	Zeitschrift des Vereins der deutschen Zucker-Industrie.
<i>Zeitsch. wiss. Photograph. Photophysik. Photochem.</i>	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.

# ANNUAL REPORTS ON THE PROGRESS OF CHEMISTRY.

## GENERAL AND PHYSICAL CHEMISTRY.

### *Evolution of the Elements.*

ALTHOUGH the phenomena of radioactivity have, in recent years, given rise to the view that certain elements are undergoing a process of degradation or disintegration with the production of elements of lower atomic weight, the reverse process has, so far, not been observed in any terrestrial phenomena. On the basis of the electronic constitution of matter, however, such a process of evolution becomes at once not only plausible, but probable. A few years ago, Professor J. J. Thomson, using the experiments of Mayer on the configurations assumed by floating magnets, showed how a periodic arrangement of the elements could be accounted for, and thus prepared the way for a theory of the evolution of the elements. This idea of evolution of elements had, of course, been put forward at an earlier date, especially by N. J. Lockyer, and during the past year A. C. and A. E. Jessup have developed this idea into a fairly consistent theory.<sup>1</sup> The spectra of the earliest nebulae consist of lines recognisable as those of hydrogen and helium, as well as two other lines not belonging to any known substance. From these four initial substances or protons, all the other elements are regarded as being evolved by the condensation round these protons (themselves formed of corpuscles) of corpuscles so as to form stable systems capable of separate existence. Whatever the exact internal structure of these atoms may be, they may be regarded as being built up of concentric "rings," or assemblages of corpuscles.

On the assumption of only four protons, the difficulty is at once met with that there are considerably more groups than protons, so that the further assumption has to be made that evolution takes place in two ways, directly and indirectly. By direct evolu-

<sup>1</sup> *Phil. Mag.*, 1908, [vi], 15, 21; *A.*, ii, 96.



tion, a product is obtained having a similar arrangement of corpuscles or "rings," and consequently similar properties; by indirect evolution, there is produced an element having a different "ring" from its antecedent, and therefore differing from it in its properties.

Dealing first with direct evolution, each ring is supposed to consist of two parts: (1) the main assemblage of corpuscles to which the ring owes its mass and shape; (2) a certain number of corpuscles which are attached to the rest in a slightly different manner, say as satellites. These the authors call "electrons." The number of such electrons gives the valency of the element. These electrons seem to possess the tendency to form systems of eight. When, therefore, direct evolution takes place, say from hydrogen, the outer ring of which contains one free electron (since hydrogen is a monad), there is an addition of one or more stable groups of eight electrons until the next member of the group, namely, lithium, is produced. This will, of course, also have one free electron, and will therefore also be univalent, and so on with the higher members of this group, which are evolved directly from lithium. Similarly, the group of the alkaline-earth metals is considered to be evolved from the second proton (proto-glucinum), and the inert elements from the proton helium, all by direct evolution. In the case of the fourth proton, proto-boron, this can give rise by direct evolution to boron, which further gives rise, by direct evolution, to aluminium, etc. It is assumed, however, that boron can also give rise, by indirect evolution, to carbon, owing to the formation of distorted rings having four electrons, and being therefore quadrivalent. These distorted rings do not consist of assemblages of eight corpuscles, but of a smaller number, the surplus corpuscles remaining free and giving a higher valence. Carbon with its distorted quadrivalent ring can undergo direct evolution with the formation of higher quadrivalent elements (silicon, etc.), or it can also undergo indirect evolution with the formation of nitrogen, oxygen, and fluorine, having distorted rings with a valency of five, six, and seven respectively. Silicon, by a similar indirect evolution, is supposed to give rise to all the elements lying between titanium and arsenic, each of which can give rise, by direct evolution, to other members of the same valency.

On the basis of this view, the authors have drawn up a new periodic table of the elements, the first portion of which may be given here.

H	p-Gl	p-B								N	O	F	He
Li	Gl	B	C							P	S	Cl	Ne
Na <sub>a</sub>	Mg	Al	Si	V	Cr	Mn	Fe	Ni	Co	Cu	Zn	Br	Kr
K	Ca	Sc	Ti							As	Se		A

Iron, nickel, and cobalt are regarded as being formed from manganese by the addition of small quantities of *matter*, whereby substances with quite abnormal rings—exhibited in the magnetic properties of the metals—are produced. These elements ought theoretically to be octavalent, but although the octavalency is not found in the case of iron, nickel, and cobalt, it becomes evident in the higher members of the iron group, ruthenium and osmium.

Owing to the existence of the abnormal rings in iron, nickel, and cobalt, and in the higher elements of these groups, it is assumed that there will be a tendency for the atoms of these elements to recover the more normal condition; and it is considered that copper, zinc, gallium, and germanium are such recovery products. Similarly, silver, cadmium, indium, and tin are the successive recovery products of ruthenium, rhodium, and palladium, whilst gold, mercury, thallium, and lead are the recovery products of osmium, iridium, and platinum. This conception is strengthened by a consideration of the electric potentials, and also by the fact that zinc, cadmium, and mercury, for example, are not connected in their refractivities. Cadmium and mercury are therefore probably not formed by direct evolution from zinc.

Besides evolution, however, devolution or degradation is also going on, and the authors discuss this question from the same point of view. As a result, they consider that the  $\alpha$ -particles are the same as one or other of the four protons.

#### *Conservation of Mass.*

The past year has seen the close of a series of laborious investigations carried out during the past decade with extraordinary skill and care by H. Landolt, with the view of testing one of the most important laws of physical science, namely, the law of the conservation of mass. Previous work in this direction, not only by Landolt but also by other investigators, pointed to the conclusion<sup>2</sup> that in the majority of the reactions studied, diminution in weight beyond the limit of experimental error occurs. The possibility of systematic errors, however, was not altogether excluded, and it was therefore necessary to re-investigate the problem more fully, and also to repeat some of the former experiments. This has now been done by Landolt.<sup>3</sup> Since, in most of the reactions investigated, heat was evolved, leading therefore to a rise of temperature and a consequent alteration in the amount of water adsorbed on the surface of the glass vessels, experiments were carried out with a view to ascertain the magnitude of this effect, and the length of

<sup>2</sup> *Ann. Report*, 1906, 3.

<sup>3</sup> *Zeitsch. physikal. Chem.*, 1908, 64, 581; see *A.*, ii, 366.

time required for glass vessels, after being suspended in a desiccator over sulphuric acid, to regain the lost moisture. This has been found to be comparatively short, not exceeding two or three days. With regard to the other effects produced by heat, however, these are found to depend not only on the kind of glass, but also on the temperature to which the vessel has been heated; moreover, the time required for the initial weight of the vessel to be attained after heating varied from about ten to twenty days. It was therefore necessary to take account of the alterations of weight due to these two causes. This has now been done in respect both of the experiments formerly carried out and of those which have now been repeated. As a result, it has been found that whereas, formerly, 75 per cent. of the reactions seemed to be accompanied by a diminution of weight exceeding the experimental error of 0.03 mgm., now, *the observed variations of weight are, in almost equal numbers, positive and negative*, and all, with four exceptions, are within the experimental error. Even in these four cases the deviations are only slightly greater than this. The final conclusion is therefore arrived at that in the fifteen reactions investigated *no change of weight can be detected*. Since the total weight employed amounted to about 400 grams, the law of the conservation of mass can be regarded as proved within the limit of accuracy of one part in ten million.

It may be mentioned that some doubt as to the correctness of the explanation of the diminution of weight given by Landolt is expressed by C. Zenghelis,<sup>4</sup> whose experiments show that certain vapours can pass through glass. He believes, therefore, that in the case of those experiments in which a considerable diminution of weight occurs, the diminution is to be attributed to loss of substance through the walls of the vessel, and not to thermal effects. This is in harmony with the fact discovered by Landolt,<sup>5</sup> that the diminution of weight did not occur when the glass vessels were coated with paraffin.

#### *The Electronic Theory in Chemistry.*

Since the electronic theory of the constitution of matter was put forward, and it was established by the study of electrical and radioactive phenomena that the cathode rays and  $\beta$ -particles constitute the unit of negative electricity, attempts have been made to formulate chemical reactions on the basis of interchange of electrons. During the past year these attempts have been carried forward by Sir William Ramsay, who, in his presidential address to

<sup>4</sup> *Zeitsch. physikal. Chem.*, 1909, 65, 841.

<sup>5</sup> *Ann. Report*, 1906, 8.

the Chemical Society,<sup>6</sup> stated the hypothesis: "Electrons are atoms of the chemical element electricity; they possess mass; they form compounds with other elements; they are known in the free state, that is, as molecules; they serve as the 'bonds of union' between atom and atom. The electron may be assigned the symbol E." In harmony with present knowledge it is also accepted that the terms "positive" and "negative" mean merely "minus electrons" and "plus electrons."

With the view of indicating the function of an electron as a chemical element, Sir William Ramsay takes the simple case of sodium chloride, which is ionised in solution into sodion and chloridion, the former positively charged (that is, having a deficiency of electrons), and the latter negatively charged. It is therefore assumed that sodion is an element which gives rise to the metal sodium by combination with an electron, whereas chloridion is a compound of an electron (really more than one electron) with an atom of chlorine. In the formation of sodium chloride, therefore, we have the reaction  $\text{ENa} + \text{Cl} = \text{NaECl}$ , the electron forming the bond of union between the sodium and the chlorine. On solution, the electron remains with the chlorine, giving chloridion. On the basis of this view of combination, the question is raised as to how the molecule of a diatomic gas, such as hydrogen, should be represented. In the ordinary symbolism, where a hyphen is used to indicate a bond of affinity (in place of the symbol E), the question is asked whether the molecule of hydrogen should be written H-H or H--H. Since the gas conducts electricity when under a low pressure, it must undergo ionisation, and it has been found that the positive ion moves more slowly than the negative. Of the various possible formulæ for the two ions thus formed, the author selects, as most probable, E and HEH.

In the case of ionising substances, no difficulty in formulation arises, but more careful consideration is necessary in the case of non-ionising substances. In compounds containing elements or groups which do not separate as ions, from which element does the electron come? Considering perchloric acid, we find that in solution the hydrogen by parting with an electron forms an ion,  $\text{H}|\text{-OClO}_3$ . "The four atoms of oxygen are capable of receiving electrons, but the chlorine atom, having already seven attached to it, can receive only one more, and that only when it is ionised, as in a solution of common salt. It then possesses its full complement of eight electrons" (the total valency being taken as eight). "Hence it follows that in perchloric acid, the electrons which form the bonds of union of the chlorine with the oxygen

<sup>6</sup> *Trans.*, 1908, 98, 774.

must be those previously associated with the chlorine, and not those associated with the oxygen." This view is in harmony with the views of Abegg<sup>7</sup> if one considers the plus sign to indicate ability to part with, and the minus sign the ability to receive, electrons. The behaviour of the complex cobaltammine nitrites can also be explained on the same basis.

The views thus put forward by Sir William Ramsay may be regarded as the translation into chemical language and notation of phenomena which are generally expressed in terms only of electricity, and, as their author states, they are put forward not as a "theory" ("a supposition which we hope may be true"), but as a "hypothesis" ("a supposition that I expect to be useful").

The discussion of the same question has also been undertaken by J. Stark,<sup>8</sup> who, for the purpose, more especially, of explaining the structure and position of band spectra (see also p. 8), puts forward the following theory of chemical combination. With regard to their union and their function, there are two kinds of negative electrons in an atom, namely, such as are united together in a ring and constitute positive electricity; and such as neutralise this positive electricity, and represent the negative valency positions of the atom. These may be called the valency electrons. They are the separable electrons. With regard to the union between the valency electron and the positive ring, three cases can be distinguished: (1) All the lines of force emanating from the valency electron end on the positive ring system of the same atom, as represented in Fig. 1. In this case the valency electron is said to be unsaturated. (2) If a second neutral atom approaches so that some of the lines of force can be deflected and end on this second atom, and, similarly, with the lines of force between the ring of the second atom and its electron, we obtain for the diatomic molecule the diagrammatic representation shown in Fig. 2. In this case we have saturated valency electrons (compare Ramsay's representation of the hydrogen molecule  $H-H$ , above). (3) Besides the strengthening of the attachment of the electron by the approach of another atom, one may also have a weakening of the attachment of certain electrons owing to the repulsion by neighbouring electrons, as indicated in Fig. 3. In this figure,  $E_1$ ,  $E_2$ ,  $E_3$ , represent saturated electrons, whilst the other three are "loosened." The first three hold the atoms together, so that it is possible for the "loosened" electrons to be split off without the molecule itself undergoing dissociation.

On the basis of these views, the following picture can be made of the electrolytic dissociation of, say, sodium chloride. The

<sup>7</sup> *Ann. Report*, 1904, 5.

<sup>8</sup> *Physikal. Zeitsch.*, 1908, 9, 85; *A.*, ii, 138.

saturated valency electron of the metallic radicle (sodium) remains attached to the non-metallic radicle (chlorine); its attachment to its own atom (sodium) is then broken, its positive spheres being saturated by the addition of neutral water molecules. We are thus led to the conclusion that electrolytic dissociation is conditioned, not merely accompanied, by the hydration of the ions produced.

This explanation of ionisation is in many points the same as that put forward some time ago by P. F. Frankland.<sup>9</sup>

Similar views with regard to chemical combination have also been

F' 1.

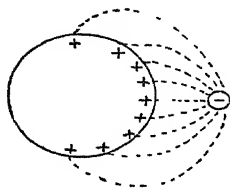


FIG. 2.

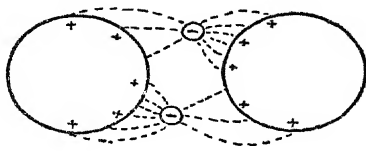
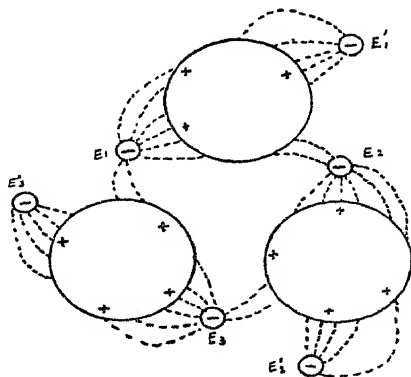
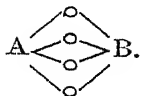


FIG. 3.



put forward by H. Kauffmann,<sup>10</sup> according to whom the single bond between two atoms of a (binary) compound will, in general, be represented by the figure  $A \langle \bigcirc \rangle B$ , where the small circle represents an electron. The figure will not, in general, be symmetrical. In the case of a double bond we should have the figure



It will be evident that here the lines of force are

<sup>9</sup> *Nature*, 1904, 70, 223.

<sup>10</sup> *Physikal. Zeitsch.*, 1908, 9, 311; *A.*, ii, 478.

forced outwards, and extend like tentacles, as it were, further out into space. These molecules will therefore be more reactive than those with a single bond.

Where more than two atoms come together, there exists the possibility that the electrons may be in union with several atoms.

Thus, for example, we may have  $A_1 \begin{array}{c} \swarrow \nearrow \\ \text{O} \end{array} A_2 \begin{array}{c} \swarrow \nearrow \\ \text{O} \end{array} A_3$ , where  $\longleftrightarrow$

represents saturated electrons,<sup>11</sup> and o a loosened electron. This corresponds with Thiele's partial valency, and it is thus seen that the divisibility of valency is demanded by the electronic theory.

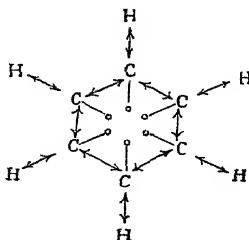
### *Spectroscopy.*

The origin of the series of line spectra of atoms has already been attributed by J. Stark<sup>12</sup> to collisions between canal and cathode rays, and the same author has, during the past year, sought to explain the origin of banded spectra on the basis of an hypothesis regarding atomic and molecular structure (see p. 6). According to the hypothesis of the author, when ionisation occurs, only valency electrons leave the atom and form free electrons. Further, the periods of the band spectra are characteristic of the valency electrons, and the banded lines are emitted by the return and recombination of the valency electrons with the positive rings. The energy which is radiated in this process is the potential energy of the valency electrons detached from the atomic rings, and this quantity is therefore fixed. By an application of Planck's law, therefore, one should obtain a *minimum* value of the wave-lengths emitted. Any particular band, therefore, which is shaded off towards the ultra-violet must have a definite limit in the ultra-violet. The author also concludes that the complete band should consist of two parts, one shaded off to the red, and the other shaded off to the ultra-violet. The only known case of this appears to be the cyanogen spectrum. In other cases only the one or the other portion is known, but this may be assumed to be due to the co-ordinated part being too deep in either the infra-red or the ultra-violet. Calculations show that for unsaturated valency electrons the band spectra lie above  $\lambda = 0.18\mu$ , and for saturated electrons above  $\lambda = 0.7\mu$ . If, therefore, a molecule has a band spectrum below  $0.7\mu$ , not belonging to an unsaturated electron, one must conclude that it contains loosened electrons. Such a substance is benzene, and the bands which are found here are to be considered

<sup>11</sup> *Cr. Stark, supra.*

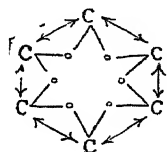
<sup>12</sup> *Ann. Report, 1906, 27.*

as due to loosened electrons. This leads to the view that the benzene molecule has the structure:



where  $\longleftrightarrow$  represents union by means of saturated valency electrons, and  $—o—$  the loosening of a valency electron. With regard to the absorption spectra of azo-compounds and quinones, there are probably also loosened electrons in connexion with the nitrogen and the oxygen which modify the spectrum.

The above formula for benzene is, however, considered by H. Kauffmann<sup>13</sup> to be unsatisfactory, and he suggests the formula:



which is a translation into electronic symbols of Thiele's formula.

### *Colour of Salts in Solution.*

The problem of the colour of salts in solution is one to which much attention has from time to time been given; and the explanations which have been put forward have depended on the particular views held with regard to the nature of solutions. Whilst it has been shown that in the case, for example, of cupric salts, the light absorption at infinite dilution is the same for different salts, and whilst a simple explanation of this can be given on the basis of the ionic theory, some obscurity still surrounds the question of colour in the case of solutions of moderate concentration. The subject has again been taken up by N. V. Sidgwick and H. T. Tizard,<sup>14</sup> who have made a direct quantitative determination of the *depth* of colour of the blue solutions of various cupric salts at varying dilutions by comparison in a tintometer with standard cupric sulphate solutions. The salts examined fall into two classes, which give very different results: (1) those of weak acids (propionate, acetate, formate, mono-

<sup>13</sup> *Loc. cit.*

<sup>14</sup> *Trans.*, 1908, **93**, 187.



chloroacetate), and (2) those of strong acids (sulphate, chloride, bromide, nitrate). The colour of the latter is much paler than that of the weak acid salts, even in the strongest solutions, and the change of colour, on dilution, is very small.

From the behaviour of weak acid salts it appears that the solutions contain at least two substances of the same blue tint, but differing in depth of colour; and, moreover, the *depth* of colour is found to depend on the nature of the anion, although the *tint* or absorption in the visible part of the spectrum is the same. The compounds in the solution may be  $\text{CuA}'$ ,  $\text{CuA}_2$ , or complex ions, such as  $\text{CuA}_4^{''}$  (where A is a univalent anion), or the products of hydrolytic dissociation or hydrates. Leaving hydrates out of account by reason of our ignorance of their constitution, it is shown that hydrolysis cannot account for the phenomena, since the addition of acetic acid to the copper acetate solutions had a comparatively slight effect on the colour. Complex ions, also, which probably give a green or brown colour to the solutions, may also be neglected, since the authors did not deal with solutions in which green made its appearance. They are therefore led to the conclusion that the molecules in solution to which the colour is due are  $\text{CuA}_2$ ,  $\text{CuA}'$ , and  $\text{Cu}''$ , the anion  $\text{A}'$  being colourless, and having, therefore, no influence on the absorption. Change of colour, therefore, on dilution, must be due to the reactions  $\text{CuA}_2 \rightarrow \text{CuA}'$  and  $\text{CuA}' \rightarrow \text{Cu}''$ . If the second change occurred to an appreciable extent, it would be expected that all the absorption curves would tend to the same point, the colour due to  $\text{Cu}''$ , but this is not the case. Further, a change in the nature of the curve might be expected at the dilution where the second reaction occurred appreciably, but no such change is found. It is therefore concluded that only the first change occurs within the limits investigated. On the basis of this assumption, a quantitative relationship can be obtained between the molecular depth of colour of the molecule  $\text{CuA}_2$ , the molecular depth of colour of the ion  $\text{CuA}'$  and the dissociation constant of the salt, and this is found to agree with experiment. It would therefore seem that the assumption made by the authors that the change of colour of solutions of weak copper salts with dilution is due to the change  $\text{CuA}_2 \rightarrow \text{CuA}'$  is correct. Further data, however, are required to confirm this.

In the case of copper nitrate solutions, experiments indicate that the complex ions have the same tint as the  $\text{Cu}(\text{NO}_3)_2$  molecule, but are deeper in colour.

The colour of salt solutions has also been studied by A. Hantzsch and his collaborators,<sup>15</sup> who have investigated the intensities of

<sup>15</sup> *Ber.*, 1908, 41, 1216; *A.*, ii, 447.

solutions of hydrogen platinichloride and sodium platinichloride at different concentrations and in various solvents. Since these substances contain the completely saturated complex  $\text{PtCl}_6$ , they are considered as being unaffected by the solvent; and it was found that equivalent solutions of the acid and the salt in the same solvent are optically identical. The molecular absorption is independent of the degree of ionisation. The solvent does not appear to exercise any influence on the absorption in the blue and violet parts of the spectrum, but does so to a very slight extent in the green and ultra-violet.

As a result of the work which has been carried out, it is concluded that (1) salts, acids, or bases with completely saturated complexes are optically unchangeable no matter whether they be ionised or not, and no matter with what colourless cation or anion they may be connected; (2) unsaturated substances, such as anhydrous salts, which become saturated on the addition of a definite number of water molecules (or ammonia), forming a saturated coloured complex, undergo a marked alteration in colour during the change; but when the complex has been completely formed, further addition of the substance combining to form the complex produces no further effect. This is seen in the case of the following reactions, for example:  $\text{CuSO}_4 \rightarrow [\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  or  $[\text{Cu}(\text{OH}_2)_4]\text{SO}_4$ .

#### *Photochemistry and Electrochemistry.*

Ninety years ago Grotthuss stated the two laws of photochemistry: (1) Only those rays of light which are absorbed can produce chemical action. (2) The action of a ray of light is analogous to that of a voltaic cell. Although the first law is generally accepted as true, the second law has met with scant attention up to the present, probably owing to the fact that until recent times our knowledge of electrochemistry was insufficient to allow it to be tested. Now, however, this is no longer the case, and the subject has received considerable attention during the past year at the hands of W. D. Bancroft,<sup>16</sup> who, in a series of papers, has not only vividly recalled the theory of Grotthuss, but has also applied it to the explanation of a number of photochemical reactions. Briefly, Grotthuss regarded light as made up of positive and negative electricity, and that its chemical action is essentially electrolytic in nature.

Although it is true that only those rays which are absorbed are photochemically active, it does not necessarily follow that all the absorbed rays are equally active or are active at all. Moreover, if

<sup>16</sup> *J. Physical Chem.*, 1908, 12, 209, 318, 417; *A.*, ii, 448, 549, 788.

the chemical action of light is electrolytic in character, it is to be expected that photochemical reactions should be capable of being produced electrolytically, and the behaviour of systems on electrolysis should also have their duplicate in photochemical changes. Even at the first glance, the similarity is seen in the effect of depolarisers. Certain reactions, for example, the reduction of ferric and cupric salts, can easily be effected by electrolysis, and for this purpose a certain minimum potential is required. This potential, however, is altered (reduced) by the presence of depolarisers. In photochemical reactions, since the electromotive force of light is low, only photochemical reactions will take place under the action of light alone which have a small decomposition voltage. But this voltage may be lowered by the addition of a suitable depolariser, and, consequently, changes which would not otherwise occur can be rendered possible. We have examples of this in the case of ferric chloride. This salt in water is practically non-sensitive to light, but in alcoholic solution it is reduced by light to ferrous chloride, the alcohol acting as a depolariser owing to the fact that chlorine readily reacts with alcohol, but not with water. Similarly, the presence of organic substances, gelatin, albumin, paper, etc., act as depolarisers in the practically important photographic processes involving silver salts. Many other light-sensitive reactions are to be regarded in the same way.

Similarly, the author shows that oxidation processes under the influence of light may be explained electrolytically, although experiments must still be made to determine whether or not the products of light oxidation and electrolytic oxidation are the same. Whether a given substance is reduced or oxidised by light, moreover, will depend on the depolariser.

The author also discusses fully the action of sensitisers. From the point of view of the Grotthuss theory, sensitisers are all depolarisers—direct or indirect. Moreover, sensitisers may be divided into optical sensitisers and chemical sensitisers. The former are depolarisers with marked absorption bands, and may therefore change the sensitiveness of the system in regard to certain rays; the latter, however, are depolarisers without marked absorption bands, and are effective by reacting chemically with the products of light action. Thus, in the case of silver bromide, the presence of a dye can alter the sensitiveness to certain light rays (as in the case of "isochromatic" photographic plates), and in this case it is the absorption band for the dyed silver bromide, not for the dyed gelatin (or carrier of the bromide), that is of importance. The Grotthuss theory requires that the sensitisers

should be depolarisers; they must be decomposed by light, and must either be reducing agents or must be converted into reducing agents by light. Thus, dyes which stain silver bromide and which are not depolarisers are not sensitisers. The sensitising action of cyanine and eosin dyes can thus be accounted for, because it has been shown that they are reduced by light.

The theory has also been applied to the explanation of chlorination and bromination of hydrocarbons, the conclusion being drawn that the action of the halogen carriers is not due to the intermediate formation of additive compounds, and that under suitable conditions the carriers react with the hydrocarbons even in the absence of free halogen. It is supposed that the halogens and the carriers give rise to ions, and that substitution takes place in the nucleus when the negative ions are present in excess, and in the side-chain when the positive ions predominate.

#### *Triboluminescence of Racemates.*

Some time ago the theory was put forward by Tschugaëff that when the two optically active forms of a compound are triboluminescent, the racemic compound is not. This has been subjected to an experimental test by D. Gernez,<sup>17</sup> who has found the statement true only in a small number of cases. Of the substances tested, those which conform to the theory are the tartaric acids, potassium tartrates, ammonium tartrates, and the sodium potassium tartrates. Exceptions to the rule, however, have been found in the case of the following: acid potassium racemate and the acid potassium tartrates; the normal tartrates and racemates of rubidium, sodium, and thallium; the acid tartrates and racemates of ammonium, potassium, rubidium, sodium, and thallium, and the double racemates of ammonium-lithium, antimonyl-potassium, caesium-lithium, lithium-potassium, lithium-rubidium, lithium-sodium, lithium-thallium, rubidium-sodium, and sodium-thallium. The *d*- and *l*-tartrates and the racemates of quinine, strychnine, and brucine, and the acid *d*- and *l*-tartrates and acid racemates of cinchonine, strychnine, and brucine, are all crystalline substances exhibiting triboluminescence. The "rule" put forward by Tschugaëff can, therefore, no longer be upheld.

#### *Osmotic Pressure.*

During the past year the important and difficult subject of osmotic pressure has again received increasing attention, and con-

<sup>17</sup> *Compt. rend.*, 1908, 147, 11 ; *A.*, ii, 748.

siderable progress has been made both in the theoretical and experimental treatment of the problem.

In continuation of previous experiments on the osmotic pressure of sugar solutions,<sup>18</sup> H. N. Morse, in collaboration with H. V. Morse, W. W. Holland, and B. Mears, has investigated the osmotic pressure of sucrose solutions at temperatures of 10° and 15°, and of dextrose solutions at 10°.<sup>19</sup> In these, several of the errors which were known or suspected in previous experiments have been eliminated in whole or in part, and the present determinations of the osmotic pressure may be regarded as accurate to the first place of decimals in the values of the pressures measured. Previous measurements had led to the belief that the osmotic pressure at 0° was substantially the same as at 20°, but it is now shown that there is undoubtedly a temperature-coefficient of osmotic pressure, and that this coefficient is practically identical with the temperature-coefficient of gases. This will be rendered obvious by the following table, which summarises the results obtained with solutions of sucrose.

*Osmotic Pressure of Sucrose Solutions.*

Concentration (weight normal).	0°.	4—5°.	10°.	15°.
0·1	2·42	2·40	2·44	2·48
0·2	4·79	4·75	4·82	4·91
0·3	7·11	7·07	7·19	7·33
0·4	9·35	9·43	9·58	9·78
0·5	11·75	11·82	12·00	12·29
0·6	14·12	14·43	14·54	14·86
0·7	16·68	16·79	17·09	17·39
0·8	19·15	19·31	19·75	20·09
0·9	21·89	22·15	22·28	22·94
1·0	24·45	24·53	25·06	25·42
Mean mol. osmotic pressure.....	23·95	24·12	24·50	24·98
Mean mol. gas pres- sure .....	22·29	22·65	23·09	23·50
Mean ratio of os- motic pressure to gas pressure .....	1·074	1·065	1·061	1·064

If one leaves out of account, at present, the measurements at 0°, which are less accurate than those at the other temperatures, especially those at 10° and 15°, it will be seen that the increase in the molecular osmotic pressure between 4—5° and 15° is 0·86 atmosphere, whilst the increase in the gas pressure is 0·85 atmosphere. The conclusion is, therefore, drawn that in weight-normal solutions the osmotic pressure of sucrose solutions between 5° and 15° obeys the Gay-Lussac law for gases. This also follows

<sup>18</sup> *Ann. Report*, 1907, 11.

<sup>19</sup> *Amer. Chem. J.*, 1908, 39, 667; 40, 1, 194; *A.*, ii, 671, 759, 1019.

from the fact that the ratio of osmotic pressure to gas pressure in this range of temperature is constant, namely, 1.065, 1.061, 1.064. These conclusions will, no doubt, be further confirmed when the osmotic pressures of solutions at 0°, 5°, and 20° have been repeated, and experiments at higher temperatures carried out.

With regard to the osmotic pressure of dextrose solutions at 10°, it is again found<sup>20</sup> that the osmotic pressure is proportional to the weight-normal concentration. But so far as experiments go at present, the temperature-coefficient of osmotic pressure is not identical with that of gas pressure, although it must also be remembered that the former experiments require to be revised in the light of more recent experience.

The laborious researches of H. N. Morse and his collaborators on the direct measurement of osmotic pressures have gradually resulted in the more or less complete elimination of the larger errors associated with such measurements, and in the perfecting of the apparatus employed. Among the improvements introduced is a new osmotic cell with improved method of attaching the manometer tube. With the new type of cell,<sup>21</sup> errors previously introduced into the measurements, due to "manometer displacement" and "distortion of stoppers," have now been eliminated. Improvements in the method of closing and also of opening the cells have also been effected, whereby other errors have been eliminated.

Direct measurements of the osmotic pressure of sucrose solutions have also been made by L. Vegard,<sup>22</sup> who employed a method similar in principle to that of the Earl of Berkeley and E. G. J. Hartley,<sup>23</sup> but with a different form of apparatus, the equilibrium point being obtained from a study of the velocity of osmosis for pressures greater and less than the osmotic pressure. The results obtained are in agreement with those obtained by Morse and Frazer and by the Earl of Berkeley and Hartley. The reversion pressure which is thus obtained, however, is dependent on the quality of the membrane, more especially as regards the occurrence of leaks—solution leak, due to mechanical defects, which does not affect the osmotic activity, and osmotic leak, due to imperfect semi-permeability of the membrane. Only when the total leak is a solution leak does the reversion pressure coincide with the actual osmotic pressure. The author has given a full mathematical discussion of this point.

Interesting work has also been done by Vegard on the properties of the copper ferrocyanide membrane prepared by electrolysis.

<sup>20</sup> Compare *Ann. Report*, 1907, 12.

<sup>21</sup> *Amer. Chem. J.*, 1908, **40**, 266; *A.*, ii, 1019.

<sup>22</sup> *Phil. Mag.*, 1908, [vi], **16**, 247, 396.

<sup>23</sup> *Ann. Report*, 1907, 15.

Elevation of temperature, it has been found, produces a great diminution in the resistance of the membrane, and the author shows that this is probably due to increase in the permeability of the membrane. The electric potential, also, under which the membrane is formed has an influence on the maximum resistance obtainable.

The experiments on osmotic pressure referred to above were not all carried out at the same temperature, and so the temperature influence could be determined. It is shown that the temperature-coefficient of the reversion pressures with different cells varies, and this is attributed to changes in the membrane. The reversion pressure, as already pointed out, coincides with the osmotic pressure only when there is no osmotic leak. It has, however, been pointed out that elevation of temperature affects the permeability of the membrane, and so gives an osmotic leak. At the higher temperatures the reversion pressures would not coincide with the osmotic pressure.

With the view of comparing the directly determined values of the osmotic pressure of solutions with those calculated from the depression of the vapour pressure, the Earl of Berkeley, in collaboration with E. G. J. Hartley and C. V. Burton, has carried out determinations of the vapour pressure and osmotic pressure of solutions of calcium ferrocyanide.<sup>24</sup> These experiments were carried out with the apparatus already described,<sup>25</sup> and the results were tested by means of a modification of the thermodynamic equation put forward by Porter,<sup>26</sup> in which the vapour pressures are referred to the conditions in air instead of in a vacuum, as in Porter's equation. When this is done, the following results are obtained, the experiments being carried out at 0°:

Concentration of solution (grams in 100 grams of H <sub>2</sub> O).	Osmotic pressure calculated from the vapour pressure, atmos.	Observed equi- librium pressure, atmos.
49.966	131.45	130.66 *
47.219	112.96	112.84
42.889	86.61	87.09
39.503	70.61	70.84
31.888	41.24	41.22

\* This may be 0.5 atmo too low.

As the above figures show, a very good agreement is obtained between the experimental values and those obtained by experiment.

Some years ago L. Kahlenberg<sup>27</sup> published the results of researches on osmotic pressure, more especially of substances in

<sup>24</sup> *Trans. Roy. Soc.*, 1908, *A*, 209, 177.

<sup>25</sup> *Ann. Report*, 1904, 11.

<sup>26</sup> *Ibid.*, 1907, 14.

<sup>27</sup> *Ibid.*, 1906, 7.

pyridine solution, using a membrane of caoutchouc, from which he concluded that the gas laws do not hold for solutions, and that previous determinations of osmotic pressure were invalid because the solutions had not been stirred. During the past year E. Cohen and J. W. Commelin<sup>28</sup> have subjected the work of Kahlenberg to criticism, and have also carried out experiments on the same lines as that investigator. From a consideration of the experimental results published by Kahlenberg, they point out that the conclusion drawn with regard to the necessity of stirring is by no means evident from the figures, since the deviations of parallel experiments are just as great when the solutions were stirred as when they were not, and, moreover, that the deviations were too great to justify the conclusion with regard to the invalidity of the gas laws. In their own experiments, Cohen and Commelin used an osmometer of about 100 c.c. capacity, and also introduced modifications into the apparatus in order to eliminate some of the errors present in the apparatus employed by Kahlenberg. Pyridine also was used as solvent and caoutchouc as a membrane, and arrangements were made whereby the solutions could be stirred. From their experiments with solutions of sucrose varying in strength from 0.1 to 0.025-N, they show that the osmotic pressure does not depend on stirring, and that in spite of all care, concordant results could not be obtained. Thus for 0.1-N solutions, pressures were obtained in one and the same apparatus of 82.3 cm. and 50.8 cm. of mercury; and in another apparatus, 67.1 cm. and 71.9 cm. These numbers, which were obtained without stirring, are by no means concordant, and are much below the theoretical value of 185.92 cm. (for the temperature of 25°). A similar lack of agreement was found even when the solutions were stirred, and, moreover, it was found (as in the case also of Kahlenberg's experiments) that a true equilibrium pressure was not obtainable, but that after a maximum had been reached the pressure fell.

The exact explanation of these results is not yet certain, but the authors show by experiment the enormous influence of moisture, whether in the pure pyridine outside or in the solution inside the vessel, and this influence is now under investigation. It will therefore be necessary to await the result of further work on pyridine solutions before they are introduced into discussions on osmotic pressure.

In connexion with the mathematical treatment of the subject of osmotic pressure, also, not a little has been published during the past year. In continuation of his investigation of the relationship between vapour pressure and osmotic pressure, as influenced by

<sup>28</sup> *Zeitsch. physikal. Chem.*, 1908, **64**, 1; *A.*, ii, 811.



the compressibility of solvent and solution, A. W. Porter<sup>29</sup> has obtained expressions for the connexion between osmotic pressure and vapour pressure for solutions of any degree of concentration, and also for any number of volatile constituents. The equation deduced by Porter has also been shown by J. E. Trevor<sup>30</sup> to be an immediate consequence of the condition of osmotic equilibrium taken in conjunction with the condition for co-existent solution and vapour and for co-existent solvent and vapour. Further, it is shown that given zero heat of dilution and constant specific volume of the solvent, there will be proportionality between the osmotic pressure and the absolute temperature.

An important contribution to the discussion of osmotic pressure has been made by H. L. Callendar,<sup>31</sup> who, after deducing formulæ for the relation between vapour pressure and the osmotic pressure, the variation of osmotic pressure with hydrostatic pressure, and the effect of pressure on the latent heat of vaporisation, discusses the various theories of osmotic pressure—gas pressure theory, surface tension theory, association or hydrate theory, and the vapour pressure theory—which have been put forward from time to time. The simple gas pressure theory put forward originally by van't Hoff for dilute solutions gives very much too low values when applied to concentrated solutions, even when the formula is modified in a manner analogous to the van der Waals equation for gases. The theory of osmotic pressure which the author now puts forward is a modification of the vapour pressure theory, the assumption being made that the ratio of vapour pressure of solution and solvent is equal to the ratio of the number of free molecules of solvent to the whole number of molecules in the solution, instead of to the number of molecules of solvent. On this view, each molecular complex is treated as a single molecule, and it is immaterial, to a first approximation, how many molecules of solvent it may contain. If each molecule of solute appropriate  $a$  molecules of solvent, and if  $n$  and  $N$  denote the whole number of molecules of solute and solvent respectively in the solution, the number of free molecules of solvent is  $N - an$ , and the whole number of molecules in solution is  $N - an + n$ . If  $p'$  and  $p''$  be the vapour pressure of solvent and solution,  $p''/p' = (N - an)/(N - an + n)$ . Assuming that the molecules of dextrose and sucrose are hydrated to a constant extent at different dilutions, and that the hydration amounts to  $a=2$  in the case of dextrose, and  $a=5$  in the case of sucrose, it is shown that the above equation gives results which

<sup>29</sup> *Proc. Roy. Soc.*, 1908, A, **80**, 457; *A.*, ii, 670.

<sup>30</sup> *J. Physical Chem.*, 1908, **12**, 141; *A.*, ii, 359. Compare Porter, *J. Physical Chem.*, 1908, **12**, 404.

<sup>31</sup> *Proc. Roy. Soc.*, 1908, **80**, A, 466; *A.*, ii 671.

are in harmony with those obtained experimentally by the Earl of Berkeley and Hartley.

With regard to the depression of the freezing point and concentration, the author points out that the ordinary formulæ neglect the change in the latent heat of fusion of ice with temperature, whereby a change in the molecular lowering of the freezing point of water by a dissolved substance undergoes change. The formula also tacitly assumes that the ratio of the difference of vapour pressures of ice and water to the vapour pressure of water is directly proportional to the temperature. The ordinary formula, therefore, does not allow of making a trustworthy comparison between theory and experiment in the case of strong solutions where the freezing point is considerably below  $0^{\circ}$ . With the help of existing data, certainly not very trustworthy, the author deduces a formula which allows of a comparison being made, and he shows that there is good agreement between the experimental and theoretical depressions in the case of solutions of sucrose when the hydration,  $a$ , is taken as 5, and of methyl and ethyl alcohol when the hydration is 1.

In the case of electrolytes, there is, of course, another complication introduced, namely, electrolytic dissociation; but if it is assumed that the number of free ions is proportional to the conductivity, the freezing-point data point to the existence of the following hydrates:  $\text{HCl}, 5\text{H}_2\text{O}$ ,  $\text{CaCl}_2, 9\text{H}_2\text{O}$ ,  $\text{MgCl}_2, 12\text{H}_2\text{O}$ ,  $\text{KCl}, \text{H}_2\text{O}$ ,  $\text{NaCl}, 2\text{H}_2\text{O}$ .

The elevation of the boiling point is discussed in a similar manner, and it is shown that sucrose has apparently the same hydration at  $100^{\circ}$  as at  $0^{\circ}$ , whereas potassium chloride and sodium chloride are more highly hydrated. With regard to the constancy of hydration on dilution, it is pointed out that on the basis of thermodynamics constant hydration can occur only when the heat of dilution is equal to zero, as is nearly the case with sucrose solutions. When the heat of dilution is not zero, then the hydration will alter with concentration, but even in the case of hydrochloric acid, which has a large heat of dilution, the change in hydration is not great.

The analysis of existing data from the point of view of Callendar's theory seems, therefore, to point to the existence in solution of definite hydrates, formed according to the laws of chemical combination, and in this respect the theory put forward is a return to the older hydrate theory as put forward by Mendeléeff, and is opposed to the hydrate theory as put forward by H. C. Jones,<sup>32</sup> according to which there exist in solution hydrates of varying composition, depending on the concentration.

<sup>32</sup> *Ann. Report*, 1907, 16.

*Aqueous Solutions.*

On the subject of aqueous solutions, much work has been done during the past year, all of which goes to show that, in all cases, hydrate formation occurs; and, in some cases, the degree of hydration seems capable of more or less accurate determination. For this purpose, several methods, besides that depending on the deviation of osmotic pressure and allied properties from the ordinary theoretical values,<sup>33</sup> have been employed. Previous investigators have shown that when a solution of an electrolyte, containing also a non-electrolyte, is submitted to electrolysis, the ratio of non-electrolyte to water at the two electrodes undergoes change; and the assumption that this change is due to the transport of water with the ions, allows one to calculate the relative degree of hydration of the ions. Further work in this direction has been carried out by E. W. Washburn,<sup>34</sup> who has determined the transport numbers for solutions of hydrogen, lithium, sodium, and potassium chlorides in presence of suitable non-electrolytes, of which the best is raffinose. Some of the results obtained by this author are given in the following table:

*Molecules of water combined with one molecule of each ion.*

Cl <sup>-</sup> .	H <sup>+</sup> .	K <sup>+</sup> .	Na <sup>+</sup> .	Li <sup>+</sup> .
0	0.28	1.3	2.0	4.7
1	0.46	2.3	3.6	7.0
2	0.65	3.3	5.2	9.3
3	0.83	4.3	6.8	11.6
4	1.02	5.4	8.4	13.9

The above figures show that the cations are all hydrated, and that the relative hydration increases with diminishing atomic weight in the case of elements belonging to the same periodic group. The actual hydration of the cation and anion would be known if the total hydration of the salt were known. From the calculations of Callendar (p. 18), this value would appear to be not very large, say less than 10. Other methods for determining the hydration of ions have also been proposed, for example, measurements of the *E.M.F.* of a cell in which the concentration of the electrolyte at the two electrodes is the same, but in which the activity of the water is altered on one side by the addition of a non-electrolyte.<sup>35</sup> No measurements have, however, been made. Reference may also be made to the boiling-point and conductivity experiments of S. M. Johnston,<sup>36</sup> who concludes that in some cases

<sup>33</sup> Compare Callendar, p. 18.

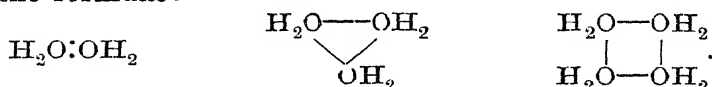
<sup>34</sup> *Tech. Quart.*, 1908, **21**, 288; *A.*, ii, 1009.

<sup>35</sup> G. N. Lewis, *Zeitsch. Elektrochem.*, 1908, **14**, 509; *A.*, ii, 805.

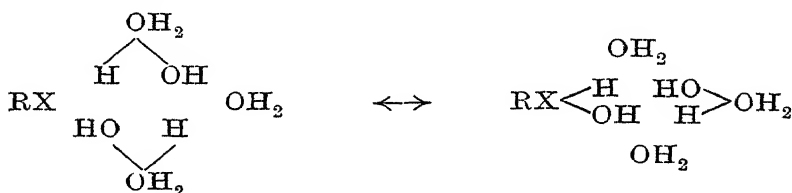
<sup>36</sup> *Trans. Roy. Soc. Edin.*, 1908, **45**, 855; *A.*, ii, 661.

both undissociated molecules and ions are hydrated, in other cases only the undissociated molecules or the ions.

In a previous Report, attention has already been called to the theory of solutions put forward by H. E. Armstrong,<sup>37</sup> and during the past year this author has given a fuller statement of the views which he has been developing during the past considerable number of years.<sup>38</sup> He considers water to be a complex mixture of active and inactive molecules, the active molecules being either simple monad hydrone,  $\text{H}_2\text{O}$ , or hydrone-hydrol (hydronol) molecules,  $\text{H}_2\text{O} \begin{smallmatrix} \text{H} \\ \diagup \text{OH} \end{smallmatrix}$ ; the inactive molecules are associated molecules, polyhydrones, the constitutions of which are represented by one or more of the formulæ:



When non-electrolytes, such as  $\text{RX}$ , are dissolved in water, they react with the hydrol and hydrone molecules, thus:



giving rise to the active complex  $\text{RX} \begin{smallmatrix} \text{H} \\ \diagup \text{OH} \end{smallmatrix}$  as well as to the inactive hydrone complex,  $\text{RX}:\text{OH}_2$ , and polymerides of the type  $\text{RX}:\text{XR}$ .

In the case of substances which give rise to composite electrolytes when dissolved in water, Armstrong assumes that not only is the compound hydrolated, but that its simple molecules also undergo distribution, so that the solution contains the isodynamic complexes:  $\text{RX} \begin{smallmatrix} \text{H} \\ \diagup \text{OH} \end{smallmatrix}$ ,  $\text{H}_2\text{O} \begin{smallmatrix} \text{R} \\ \diagup \text{X} \end{smallmatrix}$ . The occurrence of electrolysis in such solutions is dependent on influences which the composite molecules exercise reciprocally on one another while under the influence of the electric strain.

On the basis of this theory, the author discusses the various properties of solutions, such as electrolytic conductivity, hydrolysis, etc. In the case of electrolytes, the increase in the conductivity on dilution is ascribed to the increase in the proportion of effective composite molecules. In a solution of hydrogen

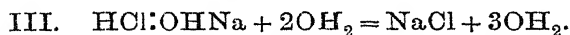
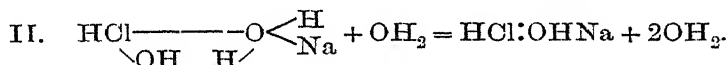
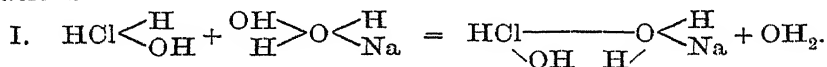
<sup>37</sup> *Ann. Report*, 1907, 21.

<sup>38</sup> *Proc. Roy. Soc.*, 1903, 81, A, 80; *A.*, ii, 814.

chloride, for example, the existence of molecules of the type  $\text{HCl} \begin{smallmatrix} \text{OH} \\ \text{H} \end{smallmatrix}$  should be favoured in weaker solutions, but in concentrated solutions the proportion of effective molecules of the type  $\text{H}_2\text{O} \begin{smallmatrix} \text{Cl} \\ \text{H} \end{smallmatrix}$  should be larger than in dilute solutions. Consequently, the conductivity in concentrated solutions is conditioned mainly by molecules of the hydrolysed solute of the type  $\text{H}_2\text{O} \begin{smallmatrix} \text{H} \\ \text{Cl} \end{smallmatrix}$ , whilst in dilute solutions it is conditioned mainly by molecules of the hydrolated type  $\text{HCl} \begin{smallmatrix} \text{H} \\ \text{OH} \end{smallmatrix}$ .

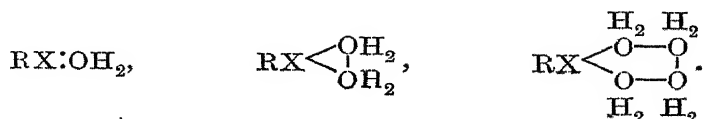
The author believes that this view gives an explanation of the fact that when solutions of sulphuric or hydrochloric acid are electrolysed, different products are obtained according to the strength of the solution, the acid system being mainly electrolysed in concentrated solutions, and the isodynamic hydrolated system in dilute solutions.

With regard to the neutralisation of acids and bases, Armstrong regards this as taking place in several stages as represented by the equations:



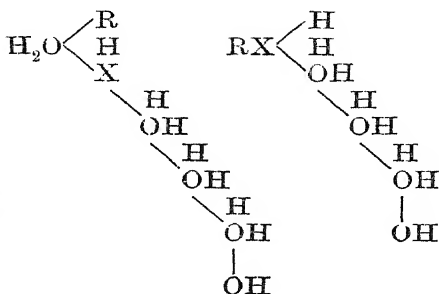
The proportion of hydrol actually set free and the amount of water formed (I and II) will depend on the amount of associated hydrol in the effective composite molecules of acid and alkali, together with the molecular proportion liberated in the final change (III) less the amount effectively associated with the dissolved salt—at most, two molecular proportions therefore. On the above view, the increase in volume which occurs on neutralisation can, in the author's opinion, be more satisfactorily explained than by the ionic theory, being a simple consequence of the different modes of combination of water before and after neutralisation.

As regards the hydration of solutes, this is regarded as being of two kinds, according as it involves hydrolation or hydronation, and compounds such as the following may be assumed:



In the case of composite electrolytes, however, the molecules of the solute may be thought of as hydrated in a way which does not deprive them of their activity, but, on the contrary, enables them to exert their influence at a distance, as in the annexed scheme.

Such chains are possibly the conveyors of the electric current in a liquid electrolyte, and must be thought of as constantly subject to attack from outside by other hydrolated molecules, and as being constantly broken down and re-made.



In connexion with the foregoing views as to the nature of solutions, Armstrong, in collaboration with others, has carried out a number of different measurements of hydrolysis and of rotations. In comparing the hydrolytic efficiency of hydrochloric, nitric, and sulphuric acids with their conductivities, Armstrong and E. Wheeler<sup>39</sup> object to the usual practice of determining conductivities in volume-normal (equivalent) solutions, and consider that weight-normal solutions should be employed. When this is done, it is found that in weight-molar solutions nitric acid is least, and sulphuric acid most, active as hydrolyst, sucrose being the hydrolyte. In tenth- and twentieth-normal molar solutions, nitric acid and hydrochloric acid are more nearly equal in activity, but sulphuric acid is much stronger than either. In the case of acids of equal conducting power, the hydrolytic activities at 25° are in the ratio  $\text{HNO}_3 : \text{HCl} : \text{H}_2\text{SO}_4 = 100 : 107 : 180$  when the activity of weight-normal nitric acid is put equal to 100.

In continuation of previous work on the determination of the average degree of hydration as determined by the influence of salts on the hydrolytic power of acids,<sup>40</sup> the differences which were met with in the hydration values, according as sucrose or as methyl acetate is used as hydrolyte, are interpreted as due to the number of hydrolated molecules present, since it is regarded that interaction takes place between these and not primarily between the nominal hydrolyte and hydrolyst. If, then, it is supposed that the affinity of methyl acetate for water is very slight, there would be relatively few effective hydrolated molecules present in a simple aqueous solution; these molecules, moreover, would be very unstable. According to the greater or less stability of the hydrolated compounds, therefore, so will be the effect of addition of a neutral

<sup>39</sup> *Proc. Roy. Soc.*, 1908, **81**, A, 95; *A.*, ii, 815.

<sup>40</sup> *Ann. Report*, 1907, 17.

salt, and consequently the apparent hydration value will vary from case to case.

The effect of non-electrolytes and of electrolytes on the rotatory power has also been studied by Armstrong and R. Whympere,<sup>41</sup> and they have interpreted the results from the standpoint of the foregoing theory of solutions.

The effect of one salt on the hydrating power of another salt present in the same solution has also been studied by H. C. Jones and C. M. Stine<sup>42</sup> by determining the freezing-point depression and the conductivity of mixed solutions. As a result, they find that when two salts are present in solution, the degree of hydration of each is altered to an extent assumed to be inversely proportional to the total hydration. Their results are not altogether in harmony with other determinations of hydration.

#### *Abnormal Dissociation Pressures.*

As is well known, the sublimation pressure of ammonium chloride was found by Brereton Baker to have the same value no matter whether the ammonium chloride was moist or dry, that is, no matter whether the salt undergoes dissociation or not. The experimental work of Baker has been confirmed by F. M. G. Johnson.<sup>43</sup> This fact, which had hitherto been received without comment, has given rise to a discussion, carried on by R. Abegg and J. J. van Laar,<sup>44</sup> which has not yet reached a definite conclusion. The former points out that according to the generally accepted theory of heterogeneous equilibrium, the concentration of the undissociated vapour ought, at constant temperature, to be independent of the presence of other gases, and therefore independent of the products of dissociation. One would expect, therefore, that since the concentration of undissociated ammonium chloride in the moist state can only be very small, there should likewise also be only a very small concentration of undissociated ammonium chloride, and therefore a very small vapour pressure, in the case of dry ammonium chloride. That a vapour pressure is obtained equal to that for the moist salt can be explained, he believes, only by the following possibilities: (1) the heat of formation of the undissociated gaseous ammonium chloride from solid ammonium chloride happens to be equal to the heat of dissociation of ammonium chloride into ammonia and hydrogen chloride; (2) the vaporous

<sup>41</sup> *Proc. Roy. Soc.*, 1908, **81**, A, 117; *A.*, ii, 817.

<sup>42</sup> *Amer. Chem. J.*, 1908, **39**, 313; *A.*, ii, 474.

<sup>43</sup> *Zeitsch. physikal. Chem.*, 1908, **61**, 458; *A.*, ii, 157.

<sup>44</sup> *Ibid.*, 455; **62**, 194, 607, 678; **63**, 623; *A.*, ii, 157, 353, 466, 569, 812.

ammonium chloride has a different molecular weight in the moist and dry states.

J. J. van Laar, on the other hand, sees in the behaviour of ammonium chloride no contradiction to the theory of equilibria, on the ground that in the case of dry ammonium chloride we are not dealing with true equilibrium but with a process of dissociation taking place with great slowness, and hastened by the catalytic action of moisture. Since there is no equilibrium between undissociated ammonium chloride and ammonia + hydrogen chloride in the case of the dry salt, and since at a given temperature, according to the kinetic interpretation, a certain number of molecules will pass from the solid into the vapour, and must be balanced by an equal number passing in the opposite direction, therefore this number will be the same whether the ammonium chloride is moist or dry. When moist, the balance is held chiefly by a re-combination of ammonia and hydrogen chloride, but in the dry state, solely by a condensation of ammonium chloride molecules. It follows, therefore, that the pressure of the ammonium chloride molecules in the dry state must be equal, not to its partial pressure in the case where moisture is present, but to the total pressure. The partial pressures are not true independent variables, as they involve the degree of dissociation, which is different in the moist and the dry systems.

It is, however, pointed out by Abegg that one is dealing with a true equilibrium, because the same value of the vapour pressure is obtained from opposite directions; and he also points out that van Laar, in his thermodynamic deduction of the equilibrium conditions, assumes that the thermodynamic potentials of the moist and dry undissociated ammonium chloride are the same, which is just the point that is under question. Further, the contention of Abegg that one should expect different values for the sublimation pressure according as dissociation does or does not occur, is confirmed by the experimental work of F. M. G. Johnson,<sup>45</sup> who has shown that the equilibrium pressure of ammonium iodide at 357° increases considerably when time is given for the slow dissociation of the hydrogen iodide produced to take place.

The position of Abegg is supported by R. Wegscheider,<sup>46</sup> who holds that the equality of sublimation pressure in the dry and moist states is possible only when the *solid* ammonium chloride is of a different nature, being probably polymorphic forms. Experiments are now in progress which will no doubt enable a definite decision of the question to be made.

<sup>45</sup> *Zeitsch. physikal. Chem.*, 1908, 65, 36; *A.*, 1909, ii, 23.

<sup>46</sup> *Ibid.*, 97; *A.*, 1909, ii, 23.



In this connexion, reference should be made to the fact that Ramsay and Young found different vapour-pressure curves in the case of some dissociating substances, according as the measurements were made by the dynamic or the static method. Attention is drawn to this by A. Smits and F. E. C. Scheffer,<sup>47</sup> who are undertaking a re-determination of the values.

### *Metastable State.*

The work carried out by H. A. Miers and his co-workers<sup>48</sup> has been extended during the past year to the study of substances which form mixed crystals. The systems investigated were those composed of naphthalene and  $\beta$ -naphthol, which form a continuous series of mixed crystals. As in previous cases, so here also, it was found that a supersolubility curve could be realised, above which crystallisation occurred only on inoculation, and below which crystallisation took place spontaneously. The range of this metastable state, however, is small, extending only to about 3°.

Similar work in connexion with aqueous solutions has also been carried out by Miss F. Isaac, on the solutions of sodium nitrate in presence of lead nitrate,<sup>49</sup> and by H. Hartley, B. M. Jones, and G. A. Hutchinson,<sup>50</sup> on solutions of sodium sulphate. These experiments all gave results similar to those obtained previously in the Oxford studies on the metastable state. From the investigations it would appear that the existence of a well-defined metastable region is a general phenomenon, but as experiments by B. M. Jones<sup>51</sup> have shown, this metastable region may become so small as practically to vanish. This was found, for example, in the case of solutions of caesium nitrate, in which the supersolubility curve was found to coincide with the solubility curve. With regard to the extent of the metastable region, also, this appears from experiments on potassium nitrate, rubidium nitrate, and caesium nitrate to diminish with increase in the molecular weight of the solute. The above order is also that of diminishing tendency to hydration, but it cannot yet be asserted definitely that this relation of the two properties is a universal one.

### *Relations between Physical Properties.*

Quite recently there has appeared the result of a very laborious examination of the relationship existing between a number of the physical properties of solvents by P. Walden.<sup>52</sup> Besides the critical

<sup>47</sup> *Zeitsch. physikal. Chem.*, 1908, 65, 70; *A.*, 1909, ii, 21.

<sup>48</sup> *Ann. Report*, 1907, 30.

<sup>49</sup> *Trans.*, 1908, 93, 384.

<sup>50</sup> *Ibid.*, 825.

<sup>51</sup> *Ibid.*, 1739.

<sup>52</sup> *Zeitsch. physikal. Chem.*, 1908, 65, 129.

comparison of data obtained by others, Walden also carried out a large number of experimental determinations of various properties of about sixteen different solvents.

1. *The Coefficient of Expansion and its Connexion with other Properties.*—A number of years ago, Mendeléeff put forward the formula for the density of a liquid at different temperatures:

$$D_t = D_0(1 - Kt),$$

or, since volume is inversely proportional to the density,  $V_t = \frac{V_0}{1 - Kt}$ , where  $K$  is the coefficient of expansion. From the experimental determinations by P. Walden and by other investigators, this formula holds for liquids with a boiling point below  $100^\circ$ , but in the case of most liquids with a higher boiling point, the formula applies over a smaller range. As regards the value of the coefficient,  $K$ , examination shows that there is no clear connexion between it and either the constitution or the molecular weight of the substance. When the values of  $K$  are compared with the boiling points of the liquids, it is found that liquids with the highest boiling points have the lowest values of  $K$ , but there is not found to be any exact parallelism between the two properties. Such a parallelism, however, is found when one compares the values of  $K$  with the critical temperatures. In this case, leaving associated liquids out of consideration, it is found that the values of  $K$  are inversely proportional to the critical temperatures, the relationship being well represented by the formula  $K\tau = 0.34$ , where  $\tau$  is the critical temperature in degrees centigrade.

This relationship has been proved over a wide range of temperature, from  $-146^\circ$  in the case of liquid nitrogen to  $+534^\circ$  in the case of diphenylmethane. It is thus found that the liquefied gases have the highest value for  $K$  (0.00392 in the case of liquid nitrogen), this value being, indeed, even greater than for gases.

The expansion coefficients are also connected with the compressibility and with the surface tension of the liquid. In the case of the latter property, there is again found to be reciprocal proportionality, and the relationship holds,  $K\gamma = 0.032$ . This is in the case, however, only of non-associated liquids.

2. *Temperature-coefficients of Surface Tension, Specific Cohesion, and Expansion.*—The change of surface tension,  $\gamma$ , and of specific cohesion,  $\alpha^2$ , with temperature has been found to agree with the formulæ  $\gamma_t = \gamma_0(1 - \beta t)$  and  $\alpha^2_t = \alpha^2_0(1 - K_1 t)$ . When, now, one compares the values of  $\beta$ ,  $K_1$ , and  $K$  (the coefficient of expansion), it is found that for non-associated liquids the temperature-coefficient of surface tension is directly proportional to the coefficient of expansion, the relationship

being expressed by the formula  $\beta = 3.45K$ . A similar parallelism exists also in the case of  $K_1$ . When the values of  $K_1$  and  $\beta$  are compared with the critical temperatures of the liquids, it is found (for non-associated liquids) that  $K_1\tau = 0.94$  and  $\beta\tau = 1.16$ . Evidently these formulæ allow of the calculation of critical temperatures from a knowledge of the temperature-coefficients  $K_1$  and  $\beta$ . The values so found agree well with those experimentally determined.

In the case of associated liquids, the values of  $K_1\tau$  and  $\beta\tau$  vary from case to case, but are in all cases smaller than in the case of non-associated liquids. The low value of the products  $K_1\tau$  and  $\beta\tau$  can, conversely, be used for the diagnosis of association.

3. *Molecular Weight, Specific Cohesion, and Absolute Boiling Temperature.*—The author has also found that the relationship holds approximately  $\frac{\text{latent heat of vaporisation}}{\text{specific cohesion}} = \frac{\lambda_\sigma}{a_\sigma^2} = 17.9$ . Both factors refer to the boiling point. If one combines this with Trouton's rule,  $\frac{M\lambda_\sigma}{T_\sigma} = 20.7$ , one obtains the relation  $\frac{M \cdot a_\sigma^2}{T_\sigma} = 1.162$ . This, also, applies only to non-associated liquids. One is therefore enabled to calculate, on the one hand, the specific cohesion at the boiling point, or, on the other, the molecular weight. Further, putting the observed value of  $\frac{M a_\sigma^2}{T_\sigma} = K$ , one can calculate the coefficient of association

from the expression  $\alpha = \frac{1.16}{K}$  in the case of associated liquids. The values obtained agree, with few exceptions, well with those obtained from the temperature-coefficient of molecular surface energy (Eötvös-Ramsay). The relationship given here had also been obtained by W. Kistiakowsky.

The relationship applies to the specific cohesion at the boiling point. By combining the above expression, however, with the equation for the temperature-coefficient, one obtains the expression

$$M = \frac{1.16 T_\sigma (\tau - 0.94t)}{a_t^2 (\tau - 0.94\sigma)},$$

where  $T_\sigma$  is the absolute boiling point,  $\sigma$  the ordinary boiling point,  $\tau$  the critical temperature,  $t$  the temperature of the experiment, and  $a_t^2$  the specific cohesion at this temperature. From this it is possible to calculate the molecular weight from readily ascertainable data.

4. *Surface Tension, Molecular Volume, and Boiling Point.*—By combining the values for specific cohesion with those of surface tension, it is deduced that  $\frac{M \cdot \lambda}{V \cdot \gamma} = 3.65$ , where  $\lambda$  = heat of vaporisation, and  $V$  is the molecular volume. Further, combining this with Trouton's

rule, one obtains  $\frac{V \cdot \gamma}{T_{\sigma}} = 5.67$ , where  $T_{\sigma}$  is the absolute temperature of the boiling point. This holds with fair approximation in the case of non-associated liquids. If one combines the expression  $\frac{M \cdot \lambda}{\gamma \cdot V} = 3.64$  with the fact that the variation in the molecular heat of vapourisation is constant, one obtains  $\frac{\Delta(\gamma V)}{\Delta t} = \text{const.}$  This is found to give equal constancy with the expression  $\frac{\Delta(\gamma V^3)}{\Delta t}$  for non-associated liquids. From the experimental values, one finds, as a mean,  $\frac{\Delta(\gamma V)}{\Delta t} = 8.80$ . Associated liquids give lower values.

### *Adsorption.*

During the past number of years, a very large amount of attention has been paid to heterogeneous or imperfectly homogeneous systems, such as are formed by fine suspensions and colloidal solutions. More especially has the distribution of substances between the colloid and the liquid medium been studied, with the result that many investigators have attributed the action of the suspended or colloid material to the formation of "adsorption compounds." In other words, the decolorising of solutions by charcoal, dyeing, etc., is supposed to be due to the dye substance being "condensed" on the surface of the suspension. The arguments which have been advanced in favour of "adsorption" have, however, been severely criticised by T. Brailsford Robertson,<sup>53</sup> who points out that there is not one of the criteria which have been put forward for adsorption compounds which does not hold equally for ordinary chemical combination in which there is a state of equilibrium. He considers, therefore, that the influence of colloids in withdrawing substances from solution is entirely due to chemical combination. This also is considered to be the case with hæmoglobin in the blood. Although recently the view has been put forward that the increase of carbon dioxide and oxygen absorption in the blood is due to "adsorption" by the colloidal material, some experiments show that, so far as the hæmoglobin is concerned, there is almost certainly chemical combination of the ordinary kind.

If adsorption or physical condensation occurs, then it should be possible to test the fact by the relationship which was deduced by Willard Gibbs,  $\Gamma = -\frac{c}{RT} \frac{d\sigma}{dc}$ , where  $\Gamma$  is the mass of the solute per square centimetre of the dividing surface in excess of what would be

<sup>53</sup> *Zeitsch. Chem. Ind. Kolloide*, 1908, 3, 49; *A.*, ii, 818.

there supposing the concentration to remain the same as in the bulk of the solution,  $c$  is the concentration in the body of the solution,  $R$  is the gas constant,  $T$  the absolute temperature,  $\sigma$  the surface tension at the interface, and  $\frac{d\sigma}{dc}$  the change of this with concentration. This equation has been put to the test by W. C. M. Lewis,<sup>54</sup> who has studied the condensation of sodium glycocholate and various dyes on the surface of drops of a liquid hydrocarbon shaken up with water. As a result, it was found that there was a considerable discrepancy between the actual amount adsorbed and that calculated on Gibbs's theory, the actual amount measured being always in excess of the theoretical values to the extent of twenty to eighty times. The reason for this discrepancy has still to be given.

ALEX. FINDLAY.

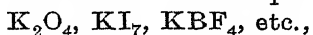
<sup>54</sup> *Phil. Mag.*, 1908, [vi], 15, 499; *A.*, ii, 357.

solution, in which true reversible equilibria subsist, behaves as a single phase towards other phases with which it is in equilibrium.

On the other hand, for equilibria within the colloidal solution, it seems to behave as a multiphase system having one more degree of freedom than that which would be assigned to it by the ordinary phase rule.

H. M. DAWSON.

tion in general) are receiving more and more the attention which they not only deserve, but require. Even at the present day it is not uncommonly taken for granted that because the compounds dealt with in organic chemistry are generally much more complex than those encountered in inorganic chemistry, therefore the problems of constitution are also much more profound; this, however, is not so, the problems in the two cases are different in their nature. In the case of organic compounds the tendency to form carbon-carbon linkings certainly leads to a great multiplicity of substances possessing high molecular weight and complicated structure, but even in such cases the comparatively simple conception of a fixed valency can be made to account for nearly all the observed facts. Carbon forms, for example, no compounds of the type  $M_2CX_6$ , although every other element in the same group does. In the study of inorganic chemistry, on the other hand, the ordinary conception of valency proves a broken reed almost from the beginning, and insistence on it tends only to hamper progress. The difficulty of giving any generally acceptable representation of the constitution of compounds such as



in spite of their apparently simple composition, shows how far we still are from possessing a workable hypothesis as to the nature of chemical combination between elements.

Seeing that the next great development of chemical theory may be expected to come from the study, not of the compounds of carbon, but of those derived from other elements, it is rather unfortunate that the difficulties to be overcome are not infrequently slurred over instead of being boldly faced, and a very large proportion of students make their first acquaintance with constitutional problems only in the domain of organic chemistry. It is somewhat difficult for those who turn their attention to the problems of modern inorganic chemistry only after they have become thoroughly imbued with the spirit of organic chemistry, to approach the subject with a sufficiently open mind; indications of the effects of this are apparent in some of the papers which appear from time to time.

During the past year the matter of valency and constitution has been dealt with from the electrochemical point of view in the Presidential Address to the Society,<sup>1</sup> and has also been the subject of several ordinary contributions to the Journal.<sup>2</sup> The subject is also treated very fully in the latest addition to the series of "Text-books of Physical Chemistry," edited by Sir W. Ramsay.<sup>3</sup> A perusal of this book shows how diverse in some

<sup>1</sup> *Trans.*, 1908, **93**, 774.

<sup>2</sup> J. N. Friend, *ibid.*, 260, 1006; H. C. Briggs, *ibid.*, 1564.

<sup>3</sup> J. N. Friend, *The Theory of Valency*.

respects have been the views propounded from time to time concerning the constitution of many of the simplest compounds, and gives an idea of the present somewhat chaotic state of affairs. Even were it only for this reason, the appearance of the work is matter for congratulation.

*The Indexing of Inorganic Substances.*

The subject of the nomenclature and classification of inorganic compounds is one of great and ever-increasing difficulty, and this has made itself felt very considerably in connexion with the preparation of a general index to the first fifty volumes of the *Zeitschrift für anorganische Chemie*, in which journal have been published so many of the results of recent investigations on complex inorganic substances. A scheme has been adopted which presents many departures from former practice, and will doubtless arouse a considerable amount of interest, and also of criticism; it is described by A. Rosenheim and J. Koppel in the preface to the recently-issued index, and also forms the subject of an appendix to a recent number of the *Zeitschrift*.<sup>4</sup> The authors point out that, at first sight, some modification of the method which Richter has so successfully applied to the indexing of organic substances might be expected to give equally good results in this department, but they state reasons why this is not so. For one thing, the chemist who has to establish the identity of some inorganic substance which he has obtained in the course of his work does not, as a rule, proceed to make first a complete ultimate analysis of it, but depends more on the results of qualitative analysis as a guide in his quest; in preparing an index, therefore, it is necessary to take into account, not merely the individual elements present in the substances, but also the well-marked radicles or groups, and an arrangement in which exact quantitative composition played an essential part would be of comparatively slight benefit. To apply Richter's method systematically to inorganic compounds, would practically mean a separate "Lexikon" for each element in turn.

The limited space which is here available does not suffice to give any adequate idea of the scheme as a whole, much less to discuss it; according to the authors, it is based primarily on: (1) the qualitative composition of the substances; (2) the valency of the individual elements; (3) the electro-affinity of the individual constituents (elements or radicles) of the compounds. In order, as far as possible, to prevent allied substances from being separated by the alphabetic order, the method of printing prefixes, like *meta-*, *per-*, *oxy-*, etc., in italics and ignoring them in the arrangement is adopted on an exten-

<sup>4</sup> *Ein Verfahren zur Registrierung anorganischer Stoffe*, 1908, 60, Lfg. 3.



sive scale. For a similar reason, names of Latin origin with terminations to indicate degrees of oxidation, etc., are entirely done away with, and in their place the ordinary name of the element is used in conjunction with numbers; thus, *magnetic oxide of iron* is to be sought under *Eisen*, and would appear as "*3-Eisen-4-oxyd*." From this example it will be seen that many names become merely paraphrases of the formulæ, and it seems a pity that the Latin names for the element have not been retained; for the present purpose, "*3-Ferrum-4-oxyd*" would serve equally well, and, by adopting this method, the symbol of the element might frequently be employed as a contraction without affecting the order, and so many of the longer names could be shortened. A system of indexing for *general* use ought to be based on names which correspond with a universally-adopted set of chemical symbols; but then we have not yet reached even this stage. Whether or not the system adopted for the present index is a success can be determined only by experience in actual use, and there has not yet been time for such a test; in any case, it may be considered an interesting experiment, and if it prove a success, or form a starting-point for the ultimate achievement of success, it will certainly constitute an important contribution to the progress attained during the past year.

#### *New Elements.*

It was mentioned in last year's Report (p. 38) that "ytterbium" had been shown by Urbain to contain two distinct elements, to which the names of *lutecium* and *neo-ytterbium* had been assigned. A similar conclusion has been reached by von Welsbach,<sup>5</sup> who proposes for the element with lower atomic weight the name *aldebaranium* (Ad = 172.9), and for the other, *cassiopeium* (Cp = 174.23). Urbain,<sup>6</sup> in giving further particulars regarding his separation, states that von Welsbach's elements are identical with those obtained by himself, and claims priority.<sup>7</sup> Whilst the occurrence of a new element in the rare-earth group thus seems definitely proved, Urbain has now shown<sup>8</sup> that, on the other hand, appearances which seemed formerly to indicate the existence of other elements were illusory; the phosphorescent spectra of Crookes' ionium and incognitum are reproduced by mixtures of salts of gadolinium and terbium, whilst Bayer's bauxium, from the bauxite of Var, was a mixture of vanadium and tungsten with traces of other known elements.

<sup>5</sup> *Monatsh.*, 1908, **29**, 181; *A.*, ii, 591.

<sup>6</sup> *Compt. rend.*, 1908, **146**, 406; *A.*, ii, 283.

<sup>7</sup> The International Committee on Atomic weights has given effect to this, and adopted the name *lutecium* (Lu = 174).

<sup>8</sup> *Compt. rend.*, 1907, **145**, 1335; *Bull. Soc. chim.*, 1907, [iv], 1, 1158; *A.*, ii, 108.

Although the evidence is at present somewhat meagre, it seems highly probable that at least one new element has been discovered in the mineral thorianite. Miss Evans,<sup>9</sup> in working through the residues from about five hundredweight of the mineral from Ceylon, obtained indications of the presence of an element giving a brown sulphide soluble in ammonium carbonate, but insoluble in hydrochloric acid, and difficult to oxidise by means of potassium chlorate and hydrochloric acid. This sulphide was separated, and by treatment with nitric acid a brown oxide was obtained, which was easily reducible by means of hydrogen, yielding, first, a black lower oxide, and finally, a dark grey, non-volatile metal. Only about fifty milligrams of the brown oxide were obtained, the yield being less than at the rate of 1 gram from a ton of the original mineral. Owing to the small quantity available, little could be done in the way of establishing the precise nature of the substance, but an attempt to determine the approximate equivalent weight of the element by reduction of the oxide in hydrogen seemed to indicate a value well above that of arsenic, with which the element may be supposed to present certain analogies.

A preliminary description of several new elements, or compounds of new elements, is also given by M. Ogawa,<sup>10</sup> who obtained them, not only from thorianite, but also from molybdenite and reinite. For one of these he proposes the name *nipponium* (Np); its equivalent weight is about 50 and atomic weight about 100, and it is therefore suggested that it may occupy a place above manganese, between molybdenum and ruthenium. It forms a basic lower oxide and an acidic higher one; the first, after ignition, is brown in colour, and the chloride formed from it gives a green solution. A second element with an equivalent weight of about 16.7 is also described as giving two oxides; the higher resembles molybdic anhydride, and forms salts of lead, barium, and silver, which are similar to the molybdates of these metals. The oxides can be reduced by hydrogen, yielding a metal which does not fuse at a red heat, which burns brilliantly in air, and is soluble in hydrochloric acid. Whether or not the element described by Miss Evans corresponds with either of these elements, or perhaps with a mixture of them, it is difficult to say at present. Ogawa obtained indications of the presence also in thorianite of a third new element, which yields a radioactive oxide.

<sup>9</sup> *Trans.*, 1908, **93**, 666.

<sup>10</sup> *J. Coll. Sci. Tōkyō*, 1908, **25**, xv, 1; xvi, 1; *A.*, ii, 952, 953.

*Atomic Weights.*

In this department there has been no very great advance during the year. In the case of the more important elements, there have been one or two re-determinations, practically repetitions of former work with improved precautions, whilst several workers have extended their investigations to some of the less prominent elements. The whole subject of atomic weights is being very fully discussed by Brauner in Abegg's *Handbuch*, and in the volume, which appeared during last year,<sup>11</sup> he contributes a general article on "fundamental" atomic weights, namely, those of sodium, potassium, silver, chlorine, bromine, and iodine, using the oxygen standard. By this method of collective treatment, instead of the individual treatment adopted for the other elements, Braune is able to give a much clearer and more concise review of these interdependent determinations. He discusses the results critically, and is not infrequently distinctly at variance with the decisions of the International Committee; his articles are well worth studying by those interested in this subject. A volume is announced, which should prove of great value to the same class of reader, and to those specially concerned with analytical chemistry; this is a collected edition of the results of the atomic weight determinations carried out by T. W. Richards and his pupils during the last twenty-one years. It is being issued in German,<sup>12</sup> and is a result of the interest aroused by the visit of Professor Richards to Berlin as "Exchange" Professor.

The two most important re-determinations during the year are those for hydrogen and for chlorine. In the former case, W. A. Noyes<sup>13</sup> has renewed experiments on the combining proportions of hydrogen and oxygen in order to test the propriety of, or eliminate the necessity for, the corrections which he had applied to his previous determinations on account of occluded gases, and which brought his value into close agreement with that obtained by Morley. The hydrogen was obtained by electrolysis, generally from dilute sulphuric acid; in some experiments it was burned directly, in others it was first absorbed in palladium; in some it was burned by means of cupric oxide, in others directly by oxygen (which was also prepared electrolytically), using palladium. In one set of experiments of this latter class, the hydrogen and oxygen were both prepared by electrolysis of barium hydroxide solution in place of dilute sulphuric acid. The results obtained in the different sets of

<sup>11</sup> *Handbuch d. anorgan. Chemie*, Bd. II, Abt. 1.

<sup>12</sup> *Experimentelle Untersuchungen über Atomgewichte* (Voss).

<sup>13</sup> *J. Amer. Chem. Soc.*, 1907, 29, 1718; *A.*, ii, 100.

experiments varied from 1.00771 to 1.00812, and give as the probable value, 1.00787; Noyes, taking this value in conjunction with that of Morley (1.00762), considers that the mean, 1.00775, would be a reasonably trustworthy value.

Noyes, along with Weber,<sup>14</sup> has also carried out a re-determination of the Cl/H ratio; the hydrogen was weighed in palladium, passed over weighed potassium platinichloride suitably heated, and the hydrogen chloride produced was collected in water, either directly or, in one set of experiments, after having first been frozen by means of liquid air. These two sets gave similar results, and in each the two values, HCl/H and Cl/H, were obtainable. The final results give Cl = 35.452 or Cl = 35.461, depending on whether the value H = 1.00762 or H = 1.00787 (see above) is taken. A set of chlorine determinations has also been made by Edgar,<sup>15</sup> who burned chlorine in an atmosphere of hydrogen, using silica-ware apparatus, and condensed the hydrogen chloride by means of liquid air; the mean results of eight experiments were: for ratio Cl/H, directly 35.194, and from ratio HCl/H, 35.193. For H = 1.00762 these give Cl = 35.462 and 35.461. This is in close agreement with the previous determinations by Dixon and Edgar, and with Guye's value deduced from the density.

The questions of the homogeneity of tellurium, and of the true atomic weight of that element, have again been the subject of investigation; all the recent work goes to confirm the view that there is not the slightest evidence of lack of homogeneity in the ordinary purified substance. Marckwald,<sup>16</sup> after several hundred systematic fractional crystallisations of 1500 grams of telluric acid, could find no difference between the first and the last fractions. Lenher<sup>17</sup> also, when converting tellurium or its oxide into chloride or double chloride, could find no difference between the element obtained from the crystallised product and that from the residues, nor could he find any between the different specimens obtained by fractional precipitation from the tetrachloride by means of ferrous salt. The two observers do not agree, however, with regard to the atomic weight of the element. Marckwald determined the proportion of tellurium dioxide obtained by the regulated heating of telluric acid, specially purified, and carefully dried to constant weight in a vacuum; in this way he obtained the value Te = 126.85, which is very decidedly lower than that obtained by Baker,<sup>18</sup> namely, 127.60, and is slightly below the

<sup>14</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 13; *A.*, ii, 371.

<sup>15</sup> *Mem. Manchester Phil. Soc.*, 1908, 52, No. 7; *A.*, ii, 577.

<sup>16</sup> *Ber.*, 1907, **40**, 4730; *A.*, ii, 33.

<sup>17</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 745; *A.*, ii, 483.

<sup>18</sup> *Ann. Report*, 1907, 36.

value for iodine. Lenher, on the other hand, from the ratio  $\text{Te} : \text{TeO}_3$ , obtained the value  $\text{Te} = 127.5$ , which is in reasonable agreement with Baker's value. In connexion with Marckwald's low result, it has been pointed out<sup>19</sup> that his method of determination is untrustworthy, owing to the practical impossibility of preparing telluric acid containing exactly the quantity of water to correspond with the formula  $\text{H}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$ . At present, therefore, the balance of evidence seems to be decidedly in favour of the anomalous positions of iodine and tellurium in the usual periodic arrangement of the elements.

A re-determination of the atomic weight of lead<sup>20</sup> has been made by the analysis of the chloride prepared by repeated crystallisation in platinum vessels from solutions containing free acid; the product did not discolour on heating, and was finally fused in an atmosphere of hydrogen chloride. The proportion of silver, as nitrate, necessary for precipitation was determined, and also the quantity of silver chloride formed; these gave closely concordant results. The mean of these gives the value  $\text{Pb} = 270.190$ , as compared with the present accepted value, 206.9.

Guye's method of calculating atomic weights from accurate determinations of gaseous densities in conjunction with the gas constants has been applied in the case of hydrogen sulphide<sup>21</sup>; the result,  $\text{S} = 32.070$ , thus obtained is an additional indication of the accuracy of the method.

New determinations of the gaseous densities of krypton and xenon have been made, and from these the values  $\text{Kr} = 83.01$  and  $\text{Xe} = 130.70$  are obtained for the atomic weights, assuming the gases to be monatomic. The former is distinctly higher, and the latter distinctly lower, than the presently accepted value, but the changes do not affect the positions of these elements relatively to others.<sup>22</sup>

Other atomic weights re-determined<sup>23</sup> are those of bismuth and palladium, but these need not be entered upon here; the values obtained are not widely different from those in present use.

### *Allotropy of Elements: Molecular Constitution.*

The relations between the different modifications of elements which can exist in more than one form, and the explanations which may be advanced as to the causes of the wide differences which these often

<sup>19</sup> Baker, *Chem. News*, 1908, **97**, 209; *A.*, ii, 483.

<sup>20</sup> Baxter and Wilson, *J. Amer. Chem. Soc.*, 1908, **30**, 187; *A.*, ii, 281.

<sup>21</sup> Baume and Perrot, *J. Chim. Phys.*, 1908, **6**, 610; *A.*, ii, 372, 940.

<sup>22</sup> R. B. Moore, *Trans.*, 1908, **93**, 2181.

<sup>23</sup> Gutbier and Birckenbach, *J. pr. Chem.*, 1908, [ii], **77**, 457; *A.*, ii, 600. Kemmerer, *J. Amer. Chem. Soc.*, 1908, **30**, 1701; *A.*, ii, 1046.

exhibit, are problems which attract an increasing amount of attention, and there seems to be a growing tendency to refer these differences to varying degrees of molecular complexity, similar to that so well known in the case of oxygen. As the other elements concerned, however, give only one kind of vapour, evidence as to differences of molecular complexity is generally wanting, and conjecture in some cases at least is allowed to take its place.

Further investigations into the nature of molten sulphur continue to be made, and, so far, A. Smith's explanation of the peculiarities exhibited by this substance<sup>24</sup> receives at least general confirmation.<sup>25</sup> The suggestion is now made by H. Erdmann<sup>26</sup> that the formation of a second distinct liquid phase is due to a partial splitting up of  $S_8$  molecules, with formation of  $S_3$  molecules. The dark variety of liquid sulphur ( $S_\mu$ ) is held to consist of these  $S_3$  molecules, because it is supposed to be a particularly reactive form of the element, and ozone, the particularly reactive form of oxygen, is known to have the composition  $O_3$ . It is even suggested that the name *thiozone* might be given to this modification, and that many polysulphides and organic sulphur derivatives might be looked upon as additive products formed by it, and should therefore be called *thiozonides* and *polythiozonides*. These assumptions are all made without any evidence whatsoever as to the molecular weight of  $S_\mu$ , and in spite of the fact that all determinations hitherto made indicate that the sulphur molecule is  $S_8$  at comparatively low temperatures, but dissociates into  $S_2$  molecules when strongly heated, giving no indication of intermediate stages. (From its effect on the freezing point of  $SA$ , Smith believes that  $S_\mu$  is also composed of  $S_3$  molecules.)

Similarly unfounded assumptions are made regarding various modifications of arsenic.<sup>27</sup> The only molecular-weight determinations for this element which have been effected lead to the formula  $As_4$ , yet not only is it suggested that various solid modifications of arsenic must be represented as  $As_3$ ,  $As_4$ ,  $As_2$ , and  $As$  respectively, but graphic formulæ for the first three are written, with single, double, and treble linkings, and a ring constitution for the first two. It is assumed that the monatomic molecule must be characteristic of the "metallic" variety, for the simple reason that typical metals are monatomic; and yet, if chemical evidence counts for anything, the "metallic" variety of carbon is presumably highly polyatomic.

<sup>24</sup> *Ann. Report*, 1907, 61.

<sup>25</sup> H. R. Kruyt, *Zeitsch. physikal. Chem.*, 1908, **64**, 513; *A.*, ii, 1028.

<sup>26</sup> *Annalen*, 1908, **362**, 133; *A.*, ii, 830.

<sup>27</sup> H. Erdmann, *Annalen*, 1908, **361**, 1; *A.*, ii, 584.

The relations between the different forms of phosphorus naturally occupy a prominent position in this section, and cause considerable discussion. But, whilst there has been a good deal of wordy warfare, little real progress has resulted. Several papers deal with the common white and red forms,<sup>28</sup> and a number of others with "Hittorf's phosphorus," which is obtained in a crystalline condition by the prolonged heating of phosphorus with lead. After a considerable amount of discussion as to the exact crystalline form of this variety of "phosphorus," it is now stated that the substance may contain fully half its weight of lead.<sup>29</sup> Supposed amorphous forms of other members of this group—antimony and bismuth—which had formerly been described as being produced by heating the crystallised metals in an atmosphere of nitrogen, are now stated<sup>30</sup> to be mixtures produced by partial oxidation of the metal, resulting in consequence of lack of purity in the nitrogen. On the other hand, the supposed crystalline form of "boron," obtained by a thermite reduction process,<sup>31</sup> always contains aluminium, and corresponds with the formula  $AlB_{12}$ ; apparently, therefore, the preparation of pure boron in a crystallised form is still unaccomplished.

Further attempts to induce the transformation of graphite into diamond, by crystallisation under very high pressures directly applied, have again been quite unsuccessful.<sup>32</sup>

The explosive varieties of the platinum metals, obtained by alloying the particular metal with a large proportion of zinc and dissolving this out from the alloy by means of acid, have now been shown to contain occluded oxygen as well as hydrogen,<sup>33</sup> so that the explosive effect is not to be referred to a sudden allotropic change, but to chemical reaction between the occluded gases. Ruthenium, however, appeared to be exceptional, as this metal was found to be explosive even when the greatest care was taken to exclude the possibility of oxygen being present.

From time to time attempts have been made to induce in other elementary gases a polymerisation analogous to the formation of ozone, but without definite result. It had been supposed that chlorine gave indications of forming a more reactive variety, but it is found that when highly purified chlorine is subjected to the

<sup>28</sup> A. Colson, *Compt. rend.*, 1907, **145**, 1167; 1908, **146**, 71, 401; *A.*, ii, 35, 176, 273.

<sup>29</sup> G. E. Linck and P. Moller, *Ber.*, 1908, **41**, 1404; *A.*, ii, 487

<sup>30</sup> E. Cohen and J. Olie, *Zeitsch. physikal. Chem.*, 1908, **61**, 586, 596; *A.*, ii, 198, 199.

<sup>31</sup> H. Biltz, *Ber.*, 1908, **41**, 2634; *A.*, ii, 762.

<sup>32</sup> R. Threlfall, *Trans.*, 1908, **93**, 1333.

<sup>33</sup> E. Cohen and T. Strengers, *Zeitsch. physikal. Chem.*, 1908, **61**, 698; *A.*, ii, 299.

influence of the silent electric discharge in an apparatus capable of indicating a change of volume of 1 in 2000, no appreciable change takes place; <sup>34</sup> the increased activity sometimes observed may be due to the presence of oxygen, which could give rise to the production of ozone or of oxides of chlorine.

### *Alloys.*

Possibly no branch of inorganic chemistry has during recent years made such rapid strides or accumulated such a mass of new and distinct observations as that which deals with the alloys of the metals and with those allied substances which for convenience may be included under the more general heading. One reason for this rapid progress is doubtless to be found in the technical demand for steels, and similar products, possessing special properties, but perhaps the chief reason has been the great improvement in appliances and processes (as, for example, in connexion with electrical heating and pyrometry), which have made investigations of this kind more accurate and more suitable for ordinary laboratory work, together with the physico-chemical developments which facilitate a proper interpretation of the observed phenomena. As is pointed out by G. Charpy <sup>35</sup> in a lecture dealing with the recent progress in connexion with one single section of the work, the system Fe-C, investigations in this field include the following branches: (a) deduction of an equilibrium diagram by the application of the phase rule, (b) thermal investigations, (c) isolation of definite compounds from the alloys by chemical processes, (d) microscopic examination, (e) observation of the physical and chemical properties of the alloys. The discussion of these various matters, as given in the lecture, is of general applicability, and might prove useful to anyone desiring a concise résumé of the subject. Certain of these branches are, of course, interesting more particularly to the physical chemist, the metallurgist, or the engineer, but the isolation of definite compounds comes very directly within the scope of the inorganic chemist, and the interest becomes still more pronounced when, as has not infrequently been the case, the systems dealt with are not those of two typical metals, but include a metal and a non-metallic or "semi-metallic" element with which distinct compounds are formed in the ordinary course. From the numerous results of quite recent work, a few illustrative examples may be selected, more or less at hazard.

Some pairs of elements, although exhibiting more or less complete miscibility in the liquid state, show no formation of definite compounds

<sup>34</sup> E. Briner and E. Durand, *Zeitsch. Elektrochem.*, 1908, **14**, 706; *A.*, ii, 940.

<sup>35</sup> *Bull. Soc. chim.*, 1908, [iv], **3**, 1; *A.*, ii, 697.



and not even of mixed crystals to any noteworthy extent; an example of this is given by the system Al-Si.<sup>36</sup> These elements mix completely in all proportions when fused, and the system gives a simple freezing-point curve of two branches, with eutectic point. In other cases the complete miscibility extends to the solid state, resulting in the formation of homogeneous alloys throughout, as in the system Fe-V.<sup>37</sup> In contrast to these, some elements which, being closely allied, might have been expected to form mixed liquids or mixed crystals, do not do so; this is the case with arsenic and bismuth, which exhibit only slight miscibility when fused, and separate completely on solidifying.<sup>38</sup>

There are numerous examples of the formation of ingredients which, from the point of view of chemical composition and otherwise, appear to be definite compounds, even in the case of elements where this was hardly to be expected; an interesting example is provided in the system Tl-Pt.<sup>39</sup> Molten thallium easily dissolves spongy platinum, and when mixtures which contain an excess of thallium are cooled, the resulting alloy shows a fine eutectic surrounding larger crystals. If the proportion of platinum is kept below 10 per cent., these crystals can easily be isolated by means of dilute nitric acid, and, when analysed, they prove to have the composition corresponding with the formula TlPt. This compound loses part of its thallium on strong heating, but retains some even at the temperature of the oxy-hydrogen flame; it displays great similarity to the analogous lead compound PbPt. Examples of this kind, of which there are many, show that in dealing with alloys the ordinary chemical equivalents (that is, electrochemical equivalents) have no general significance. The isolation of compounds is often a very difficult problem, owing to the lack of suitable solvents, which, while attacking the other ingredients, will not also attack the compound itself. A good example of such a difficulty being successfully overcome is provided by the isolation of magnesium silicide,  $Mg_2Si$  (which is decomposed even by water), from an alloy rich in magnesium; the excess of metal in this case was removed by treatment with a mixture of ethyl iodide and ether.<sup>40</sup>

In the case of "alloys" derived from elements like sulphur, selenium, phosphorus, etc., which with metals form compounds of the ordinary type, the results obtained by the methods under consideration are often much less simple than might be expected; at the high

<sup>36</sup> W. Fraenkel, *Zeitsch. anorg. Chem.*, 1908, **58**, 154; *A.*, ii, 592.

<sup>37</sup> R. Vogel and G. Tammann, *ibid.*, 73; *A.*, ii, 502.

<sup>38</sup> K. Friedrich and A. Leroux, *Metallurgie*, 1908, **5**, 148; *A.*, ii, 148.

<sup>39</sup> L. Hackspill, *Compt. rend.*, 1908, **146**, 820; *A.*, ii, 504.

<sup>40</sup> P. Lebeau and R. Bossuet, *ibid.*, 282; *A.*, ii, 184.

temperatures of fusion, known compounds may become unstable and new compounds be produced, with proportions totally different from the others. Thus, the only nickel sulphide that is stable in contact with the liquid phase of the system Ni-S is the compound  $\text{Ni}_3\text{S}_2$  (at atmospheric pressure the maximum amount of sulphur present is 31 per cent., owing to volatilisation), but, on cooling, transformations, take place in the solid, and the existence of the three compounds  $\text{NiS}$ ,  $\text{Ni}_3\text{S}_4$ , and  $\text{NiS}_2$ , is clearly indicated; there is no  $\text{Ni}_2\text{S}$ , although a compound,  $2\text{FeS}, \text{Ni}_3\text{S}$ , can be formed when iron is present.<sup>41</sup>

A few years ago it was found that certain alloys, although formed from non-magnetic elements, are very distinctly magnetic, and considerable attention is now devoted to the observation of this property; as noted elsewhere, it has now been found that some nitrides, or alloys of nitrides with excess of the metal, are magnetic in a very pronounced degree.

A branch of investigation, very closely allied to the study of alloys, deals with the problem of the separation of silicates and similar substances from fused magmas, and a fair amount of work is being steadily accomplished in this connexion. The subject is of great interest petrologically, from the bearing which it has on the solution of problems concerning the formation of igneous rocks, etc. The same general methods are also occasionally used to throw light on other questions; thus it has recently been shown that selenium and iodine form neither compounds nor mixed crystals;<sup>42</sup> also, that sulphur and iodine form no compounds, and give only one series of mixed crystals, containing only moderate percentages of sulphur. This is a matter of some interest in connexion with the effect of iodine on the equilibrium between  $\text{S}\lambda$  and  $\text{S}\mu$ .<sup>43</sup>

### *Reduction of Oxides, etc.*

The reduction of certain metallic oxides by mere raising of the temperature is a chemical process to which the student is very early introduced, but until quite recently very little attention was paid to this matter as a general phenomenon, and it was only in isolated cases that the reversibility of oxidation processes and the part played by the oxygen concentration in the surrounding atmosphere were properly taken into account; as a rule, also, the cases specially considered from this point of view were those in which reduction takes place from a higher

<sup>41</sup> K. Bornemann, *Metallurgie*, 1908, 5, 13, 61; *A.*, ii, 292.

<sup>42</sup> G. Pollini and S. Pedrina, *Atti R. Accad. Lincei*, 1908, [v], 17, ii, 78; *A.*, ii, 833.

<sup>43</sup> F. Ephraim, *Zeitsch. anorg. Chem.*, 1908, 58, 338; *A.*, ii, 581.

to a lower oxide only, the case of mercury being treated as exceptional with regard to the reversibility of the action between metal and oxygen. In view of a number of recent experimental investigations, however, it is becoming necessary to deal with the question in a more general and comprehensive manner; the results obtained show that many "stable" oxides can easily undergo dissociation at not very high temperatures if the other conditions are suitable, that is, provided the pressure or concentration of oxygen be kept sufficiently low. For example, in the cathode light vacuum,<sup>41</sup> cadmium oxide at 1000° dissociates into metal and oxygen, lead oxide does so at 750°, and bismuth oxide at a still lower temperature; some sulphides also dissociate, giving sulphur and metal or lower sulphide. For a number of oxides the dissociation pressures at various temperatures have been measured,<sup>45</sup> and where possible also the temperatures have been ascertained at which the pressure reaches that of oxygen in the air, this being, of course, the temperature at which decomposition would set in under ordinary conditions. One example may be cited: In air, cupric oxide would begin to decompose in the neighbourhood of 1025° with formation of oxygen and cuprous oxide; but this is a much more stable compound, for even at that temperature its dissociation pressure is not more than 1 mm. Other determinations of a more or less similar kind have been made by other observers regarding the oxides of chromium (alone, and in presence of copper oxides),<sup>46</sup> manganese,<sup>47</sup> iron,<sup>48</sup> and iridium.<sup>49</sup>

In view of the dissociation phenomena just referred to, the mechanism of the reduction of oxides by means of, say, carbon would appear to be uncertain; is the oxide directly attacked by the reducing agent, or does this merely act as a kind of absorbent for the oxygen liberated by dissociation? This problem also has been recently investigated,<sup>50</sup> and it would appear that, in many cases at least, carbon acts directly on the oxide; evolution of gas takes place at temperatures far below those at which direct dissociation can be detected in absence of carbon. It has recently been satisfactorily proved that even magnesium oxide can be reduced by carbon at a temperature of 1700°; this had previously been surmised from observed facts,<sup>51</sup> but has now

<sup>41</sup> Damm and Krafft, *Ber.*, 1907, **40**, 4775; *A.*, ii, 39; see also W. von Bolton, *Zeitsch. angew. Chem.*, 1906, **19**, 1537.

<sup>45</sup> H. W. Foote and E. K. Smith, *J. Amer. Chem. Soc.*, 1908, **30**, 1344; *A.*, ii, 847.

<sup>46</sup> L. Wohler and P. Wohler, *Zeitsch. physikal. Chem.*, 1908, **62**, 440; *A.*, ii, 387.

<sup>47</sup> R. J. Meyer and K. Rotgers, *Zeitsch. anorg. Chem.*, 1908, **57**, 104; *A.*, ii, 191.

<sup>48</sup> P. T. Walden, *J. Amer. Chem. Soc.*, 1908, **30**, 1350; *A.*, ii, 852.

<sup>49</sup> L. Wohler and W. Witzmann, *Zeitsch. Elektrochem.*, 1908, **14**, 97; *A.*, ii, 301.

<sup>50</sup> H. C. Greenwood, *Trans.*, 1908, **93**, 1483.

<sup>51</sup> Lebeau, *Compt. rend.*, 1907, **144**, 799; *A.*, ii, 1907.

been demonstrated very conclusively<sup>52</sup> by dissolving the resulting magnesium vapour in metallic copper (which itself has no action on magnesia), and, still more conclusively, by condensing it as a metallic mirror on the walls of an evacuated glass vessel.

A study of the rates of reduction of the oxides of lead, cadmium, and bismuth by means of carbon monoxide demonstrates clearly that lower oxides of these metals exist as definite compounds, a matter which formerly was in some doubt.<sup>53</sup> When the results are plotted, breaks in the resulting curves indicate very clearly the formation of the compounds  $\text{Pb}_2\text{O}$ ,  $\text{Cd}_2\text{O}$ , and  $\text{BiO}$ . From results obtained by a totally different method, it appears, further, that these are basic oxides, yielding ions in solution; this method consists in showing that the ordinary salt solutions can dissolve and re-deposit the appropriate metal. It is known, for example, that when copper is brought into contact with solution of cupric sulphate, an equilibrium,  $\text{Cu} + \text{CuSO}_4 \rightleftharpoons \text{Cu}_2\text{SO}_4$ , is established; rise of temperature shifts this quite appreciably towards the right, and a hot solution deposits copper on cooling.<sup>54</sup> By arranging a circulation apparatus, in which solution of a suitable salt was brought into contact with metal at a heated part and was then cooled at another, deposits of metal were obtained in the case of lead, cadmium, bismuth, and thallium.<sup>55</sup> These experiments, whilst pointing distinctly to the formation of lower salts, give no evidence as to the composition of these, but it may be taken for granted that in the first three cases they correspond with the oxides referred to above. With regard to thallium, however, the matter is not so simple; the ion of the thallos salts is  $\text{Tl}^+$ , and a lower salt would therefore involve the assumption of a compound ion,  $\text{Tl}_2^+$ ; this would present a certain analogy to the anion of the periodides,  $\text{I}_3^-$ . The preparation in the solid state of halogen compounds derived from a lower oxide of bismuth has actually been effected by the action of the metal on the ordinary halides. It is stated<sup>56</sup> that in this way a dichloride,  $\text{BiCl}_2$ , can be obtained in distinct crystals, which are less dense than an equivalent mixture of metal and trichloride would be, and therefore must consist of a true compound; the analogous bromide and iodide were also obtained. On the other hand, a physico-chemical study of the whole system, bismuth-chlorine, leads to the conclusion that  $\text{BiCl}_2$  does not exist, but that  $\text{BiCl}$  and  $\text{BiCl}_4$  do;<sup>57</sup> on similar grounds, the existence of a bromide,  $\text{BiBr}$ , is upheld.

<sup>52</sup> R. E. Slade, *Proc.*, 1907, **23**, 152; *Trans.*, 1908, **93**, 327.

<sup>53</sup> F. J. Brislee, *Trans.*, 1908, **93**, 154.

<sup>54</sup> *Ann. Report*, 1907, 45.

<sup>55</sup> H. G. Denham and A. J. Allmand, *Trans.*, 1908, **93**, 424, 833.

<sup>56</sup> W. Herz and A. Guttmann, *Zetsch. anorg. Chem.*, 1908, **56**, 422; *A.*, ii, 198.

<sup>57</sup> B. G. Eggink, *Zetsch. physikal. Chem.*, 1908, **64**, 449; *A.*, ii, 1043.

Although they scarcely fall within this section, two other cases of new derivatives being obtained may be mentioned here. A lower oxide of titanium,  $\text{TiO}$ , has been recorded, but analogous derivatives were practically unknown; the di-iodide,  $\text{TiI}_2$ , which has now been prepared as a distinctly crystalline substance,<sup>58</sup> is the first definite example of these. It is obtained by passing the vapour of the tetra-iodide over heated mercury in an atmosphere of hydrogen, and, being less volatile than the tetra-iodide and mercuric iodide, is easily obtained separately from these in the form of black lamellæ. It is insoluble in organic solvents, and is decomposed by water and aqueous solutions.

The other new compounds referred to are a hydrated sesquioxide of palladium (which is thus brought more into line with its two neighbours, rhodium and ruthenium), and substances derived from it;<sup>59</sup> in the meantime, although the stage of oxidation is known, the exact composition of the hydroxide itself is not known, and it must be represented by the formula  $\text{Pd}_2\text{O}_3, x\text{H}_2\text{O}$ . It is obtained by electrolytic oxidation of palladous nitrate, and separates as a brown precipitate at the anode; the temperature must be kept low, and certain other precautions observed. The process can easily proceed beyond the desired stage, not so much by direct oxidation as by the action of acid, giving dioxide and palladous salt. The new oxide dissolves easily in hydrochloric acid, forming a chloride which is unstable; but by suspending the oxide in ether along with rubidium chloride or caesium chloride, cooling with solid carbon dioxide and ether, and then passing in hydrogen chloride, crystalline compounds of the composition  $\text{M}_2\text{PdCl}_5$  can be prepared. These are decomposed by water, giving derivatives of the lower chloride; no potassium derivative could be obtained.

A striking and peculiar phenomenon involving oxidation and reduction has been observed in connexion with certain vanadium compounds of the alkali metals and of silver.<sup>60</sup> When any of these compounds is heated to a high temperature in air and then allowed to cool, it is found that "spitting" takes place, similar to what is so well known in the case of molten silver; here, also, the effect is due to the escape of oxygen. It has been proved that, at the high temperature, vanadates are formed corresponding with the general formula  $\text{M}_2\text{O}, x\text{V}_2\text{O}_5$  (where  $x$  ranges in value from 2 to 6), but that these, on cooling, change into double vanadyl vanadates of various compositions, part of the  $\text{V}_2\text{O}_5$  becoming  $\text{V}_2\text{O}_4$  with loss of oxygen; this oxygen is re-absorbed when the vanadyl derivatives are again heated in air.

<sup>58</sup> E. Defacqz and H. Copaux, *Compt. rend.*, 1908, **147**, 65; *A.*, ii, 699.

<sup>59</sup> L. Wohler and F. Martin, *Zeitsch. anorg. Chem.*, 1908, **57**, 398; *A.*, ii, 392.

<sup>60</sup> W. Prandtl and H. Murchhauser, *ibid.*, 1907, **56**, 173; *A.*, ii, 46.

*Peroxides, "Per-salts," etc.*

The various substances which may be conveniently classed together under the above heading present many points of general interest, and provide problems for many of which no very satisfactory solution has been propounded. This is reflected in the fairly considerable amount of recent work in connexion with them.

One had thought that the constitution to be assigned to the members of the two groups of higher oxides, commonly designated as peroxides and exemplified by, say,  $\text{MnO}_2$  and  $\text{BaO}_2$ , had been fairly satisfactorily settled, as expressed by the general formulæ  $\text{M} \leq \text{O}$  and

$\text{M} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$ ; the former are oxides of the ordinary type, possessing feebly basic properties (capable of yielding an ion  $\text{M}^{+++}$ ) or feebly acidic properties, or possibly both, whilst the latter are "salts" of hydrogen peroxide. (The expression *peroxidate* seems to be coming into use, and is in many respects convenient.) It is now suggested, however,<sup>61</sup> that the two best-known members of the first group, namely  $\text{MnO}_2$  and  $\text{PbO}_2$ , cannot possess a similar constitution, and that the lead compound should be represented by the formula  $\text{Pb} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$ . It is rather

difficult to see what particular character this formula is intended to express; it would seem to indicate a novel kind of peroxidate, but lead dioxide does not yield hydrogen peroxide. The only reason adduced for assigning different constitutions is the fact that manganese dioxide yields dithionate when treated with sulphurous acid, whilst lead dioxide does not. In view of the great resemblances between the two oxides, this reason appears totally inadequate, unless there is no other way out of the difficulty; one simple explanation would be to assume that, whilst manganese dioxide forms a normal sulphite,  $\text{Mn}(\text{SO}_3)_2$ , which rearranges to form manganous dithionate,  $\text{MnS}_2\text{O}_6$ , lead dioxide forms a *basic* sulphite,  $\text{PbOSO}_3$ , which rearranges to form lead sulphate,  $\text{PbSO}_4$ .

The possible existence of a definite higher oxide of silver has often formed the subject of investigation, and still continues to do so; in last year's Report (p. 46), facts in favour of assuming an oxide,  $\text{AgO}$ , yielding a cation,  $\text{Ag}^{++}$ , were discussed. According to the evidence obtained from electrochemical determinations,<sup>62</sup> it would now appear that whilst only the oxide,  $\text{AgO}$ , can be obtained by electrolytic oxidation in presence of alkali, with acid electrolyte both this and a still higher oxide,  $\text{Ag}_2\text{O}_3$ , can be produced, each corresponding with a

<sup>61</sup> Marino, *Zeitsch. anorg. Chem.*, 1907, 56, 233; *A.*, ii, 106.

<sup>62</sup> Luther and Pokorný, *ibid.*, 1908, 57, 290; *A.*, ii, 277.

definite electrolytic potential. The establishment of the existence of two higher oxides of silver—not peroxides—is interesting, and brings this metal into closer agreement with its neighbours in the first group of elements, with copper through the oxide  $\text{Ag}_2\text{O}$ , and with gold through  $\text{Ag}_2\text{O}_3$ . This oxide shows a great tendency to adsorb silver salts, and so gives rise to the various indefinite substances which at different times have been described as silver peroxide. According to other workers,<sup>63</sup> the dark anodic deposit formed during the electrolysis of silver nitrate solution is silver pernitrate,  $\text{AgNO}_4$ , which decomposes with formation of these indefinite “peroxides.”

Reference may here be made to a new oxide of thallium which has been prepared,<sup>64</sup> corresponding in composition with the formula  $\text{TlO}$ ; this substance illustrates very well the problems in isomerism which may arise even in connexion with comparatively simple inorganic substances. The oxide is obtained at a low temperature by the action of hydrogen peroxide on a solution of thallous sulphate and potassium hydroxide; a red precipitate forms at first, but this rapidly changes into a bluish-black substance having the above composition. Three possible views might be held as to the nature of such a mixture. In view of the known molecular weight of indium dichloride,  $\text{MCl}_2$ , the existence of a simple oxide,  $\text{Tl}_2\text{O}$ , is at first sight not improbable; taking into account merely the method of preparation a thallous peroxide,  $\text{Tl}_2\text{O}_2$ , analogous to sodium peroxide would seem a likely product; whilst the generally accepted views regarding many thallium compounds with halogens, etc., would point to a thallous thallic oxide,  $\text{Tl}\cdot\text{O}\cdot\text{Tl}\cdot\text{O}$ , as being highly probable. The most generally satisfactory assumption to make would be that thallous peroxide is produced in the first instance, but rapidly rearranges into the double oxide; this would be analogous to the change which thallous persulphate,  $\text{Tl}_2\text{S}_2\text{O}_8$ , undergoes into the isomeric thallous-thallic sulphate,  $\text{Tl}\cdot\text{Tl}\cdot(\text{SO}_4)_2$ .

Further evidence regarding the action of hydrogen peroxide on mercury and the formation of mercury peroxide<sup>65</sup> is given by von Antropoff<sup>66</sup>; he also comes to the conclusion that  $\text{HgO}_2$  is mercuric peroxide, and suggests that probably a still less stable mercurous peroxide,  $\text{Hg}_2\text{O}_2$ , is also formed when hydrogen peroxide and mercury interact.

The formation and decomposition of hydrogen peroxide itself continue to be investigated. Nernst's view that its formation in flames is not due to the combustion process, but is merely the result of the exposure of water vapour (with or without free oxygen) to high

<sup>63</sup> Baborovsky and Kuzma, *Zeitsch. Elektrochem.*, 1908, **14**, 196; *A.*, ii, 378.

<sup>64</sup> Rabe, *Zeitsch. anorg. Chem.*, 1908, **58**, 23 *A.*, ii, 498.

<sup>65</sup> *Ann. Report*, 1907, 49. <sup>66</sup> *J. pr. Chem.*, 1908, [ii], **77**, 273; *A.*, ii, 383.

temperature, followed by rapid cooling, is confirmed by the observations of F. Fischer and O. Ringe,<sup>67</sup> who succeeded in showing the formation of peroxide when the heating was effected by means of (a) a Nernst filament, (b) a capillary tube of magnesia, heated in a flame, (c) a hydrogen flame directly, (d) electric spark discharge; this last result is contrary to Nernst's statement, and was secured by maintaining a greater velocity of the current of steam and oxygen so as to ensure more rapid cooling. A patent<sup>68</sup> has been secured for the actual preparation of hydrogen peroxide by the method of blowing various mixtures of steam, hydrogen, and oxygen through flames or other suitable sources of heat, the velocity being not less than one metre per second; or the source of heat may be caused rapidly to rotate in the mixture.

According to Abel,<sup>69</sup> the catalysis of hydrogen peroxide by iodine or iodides is due to the occurrence of the two reactions: (1)  $\text{H}_2\text{O}_2 + \text{I}_2 = 2\text{H}^+ + 2\text{I}' + \text{O}_2$  and (2)  $\text{H}_2\text{O}_2 + 2\text{I}' + 2\text{H}^+ = 2\text{H}_2\text{O} + \text{I}_2$ . The first is greatly accelerated by alkalis, the second by acids, and by maintaining in the solution a suitably small concentration of hydrogen ions (addition of acetic acid and sodium acetate), the two may be made to proceed at the same rate, so that then the only apparent change is the liberation of oxygen. The second of Abel's equations might be represented as (a)  $\text{H}_2\text{O}_2 + 2\text{I}' = 2\text{HO}' + \text{I}_2$  and (b)  $2\text{HO}' + 2\text{H}^+ = 2\text{H}_2\text{O}$ ; (1) and (a) together, then, represent more clearly the two chief modes of action of hydrogen peroxide, reducing or oxidising, according as division of the molecule takes place between the hydrogen and oxygen, or between the oxygen atoms themselves (whilst the alternation of both results in apparently simple decomposition). This behaviour can to a certain extent be compared to that of an "amphoteric" metallic hydroxide, such as that of zinc, towards alkali and acid respectively:

$$\text{Zn} \begin{array}{c} \text{O} \text{H} \\ \text{O} \text{H} \end{array} \begin{array}{c} \text{H} \\ \text{H} \end{array} \begin{array}{c} \text{HO} \\ \text{HO} \end{array} \begin{array}{c} \text{K} \\ \text{K} \end{array} \text{ and } \text{Zn} \begin{array}{c} \text{OH} \\ \text{OH} \end{array} \begin{array}{c} \text{H} \\ \text{H} \end{array} \begin{array}{c} \text{Cl} \\ \text{Cl} \end{array}$$

The catalysis of hydrogen peroxide is apparently not influenced by the concentration of the dissolved oxygen present, at least when a colloidal solution of a noble metal serves as catalyst; the rate of decomposition has been measured under very considerable oxygen pressures,<sup>70</sup> and up to as high as 200 atmospheres no difference could be found.

The formation of ozone (which we may here treat as a peroxide) from oxygen by means of the silent electric discharge can be rendered more and more complete by lowering the temperature, and it has been

<sup>67</sup> *Ber.*, 1908, **41**, 945; *A.*, ii, 370.

<sup>68</sup> D.R.-P. 197023; *A.*, ii, 829.

<sup>69</sup> *Zeitsch. Elektrochem.*, 1908, **15**, 598; *A.*, ii, 939.

<sup>70</sup> Spear, *J. Amer. Chem. Soc.*, 1908, **30**, 195; *A.*, ii, 370.



found possible,<sup>71</sup> by maintaining the apparatus at the temperature of liquid air (at which temperature the vapour pressure of ozone is exceedingly slight), to convert 99 per cent. of the oxygen into ozone. Even at this temperature the spark discharge gives less than 1 per cent. of ozone, and this small amount may be due really to accompanying silent discharge.

In last year's Report (p. 61) mention was made of the preparation of a new barium percarbonate,  $\text{BaCO}_4$ ; additional particulars concerning this salt have now been published, and also a description of the preparation of a series of related sodium percarbonates.<sup>72</sup> The formation and decomposition of the barium salt play an important part in the preparation of hydrogen peroxide by the interaction of hydrated barium peroxide and carbonic acid; if this action is brought about in presence of a suitable proportion of water and at a low enough temperature, almost no hydrogen peroxide is liberated until more carbonic anhydride has been passed in than is equivalent to the barium present, but thereafter the formation is very rapid. The carbon dioxide apparently first unites directly with the barium peroxide, and forms a yellow solid of the composition represented by the above formula, but it has not yet been obtained free from water; the compound is not rapidly decomposed by water, nor does either alcohol or ether remove hydrogen peroxide from it, so that it does not seem to be merely an additive compound of the latter substance. It is quickly decomposed by acids, including carbonic acid, with formation of hydrogen peroxide. The sodium salts have been obtained in a somewhat similar manner from sodium peroxides, in presence of a suitable proportion of water and at low temperatures, by addition of gaseous or solid carbon dioxide. The peroxides used were  $\text{Na}_2\text{O}_2$ ,  $\text{Na}_2\text{O}_3$ , and  $\text{NaHO}_2$ ; it is stated that this last can be obtained in two isomeric forms, namely,  $\text{NaO}\cdot\text{OH}$  and  $\text{O}\cdot\text{Na}\cdot\text{OH}$ , the former by the action of hydrogen peroxide on sodium ethoxide, and the latter, as described by Tafel,<sup>73</sup> by the action of absolute alcohol on  $\text{Na}_2\text{O}_3$ . The salts obtained, having the composition indicated by the formulæ, are designated as follows: sodium dioxide carbonate,  $\text{Na}_2\text{CO}_4$ ; sodium dioxide bicarbonate,  $\text{Na}_2\text{C}_2\text{O}_6$ ; sodium trioxide carbonate,  $\text{Na}_2\text{CO}_5$ ; sodium trioxide bicarbonate,  $\text{NaHCO}_4$  (two isomerides, one from each of the isomeric sodium hydrogen dioxides). The names are evidently taken merely from the name of the oxide used in the preparation; what the probable constitution of the compounds is remains to be seen, and

<sup>71</sup> Briner and Durand, *Compt. rend.*, 1907, **145**, 1272; *A.*, ii, 101.

<sup>72</sup> Wolfenstein and Peltner, *Ber.*, 1908, **41**, 275, 280; *A.*, ii, 180, 183; *D.R.-P.* 188569, 196369; *A.*, ii, 180, 830.

<sup>73</sup> *Ber.*, 1894, **27**, 2297; *A.*, 1894, ii, 448.

there must at present be considerable doubt even as to the true composition. Substances of so unstable a nature as these are, which cannot be crystallised or otherwise purified, may quite well be mixtures containing carbonate and a percarbonate in various proportions; the substance  $\text{NaHCO}_4$  might be  $\text{Na}_2\text{C}_2\text{O}_6 + \text{H}_2\text{O}_2$ , and so on. The assumed existence of two isomeric substances corresponding in composition with the formula  $\text{NaHCO}_4$  is based merely on observed differences in the degree of stability, and this by itself is, of course, not very conclusive evidence; this also constitutes the only evidence for the existence of isomeric peroxides. No definite indication can be given as to whether  $\text{Na}_2\text{C}_2\text{O}_6$  is the analogue of the potassium salt obtained electrolytically. Possibly the further investigations in which the authors are engaged may enable them to clear up some of these points.

The preparation of crystalline sodium perborate<sup>74</sup> can be conveniently effected by first saturating with carbon dioxide a 50 per cent. solution of sodium peroxide, adding a sufficiency of a saturated solution of sodium metaborate, and then cooling almost to zero.

Indications have been obtained of the formation of small quantities of perstannates by the electrolysis of concentrated solutions of alkali stannates,<sup>75</sup> but the compounds are very unstable, and the solutions soon decompose.

In a paper dealing with columbium and its compounds,<sup>76</sup> C. W. Balke and E. F. Smith describe several new well-crystallised salts of percolumbic acid,  $\text{H}_3\text{CbO}_8$ , which represents one of the most highly oxidised sets of compounds known. Of the salts mentioned, the most interesting from the theoretical standpoint are the rubidium and caesium salts,  $\text{Rb}_3\text{CbO}_8$  and  $\text{Cs}_3\text{CbO}_8$ ; being anhydrous, they indicate quite clearly that the high degree of oxidation of this class of salt cannot be referred to additive compounds with hydrogen peroxide. In the present state of our knowledge, these substances are most conveniently looked upon as columbates in which every atom of oxygen has been replaced by the peroxide group,  $-\text{O}\cdot\text{O}-$ , an assumption which is in accord with their mode of preparation by the action of hydrogen peroxide. The salts lose exactly half of their oxygen on ignition, and leave ordinary ortho-columbates.

The formation and reactions of the persulphates continue to form the subject of a considerable amount of original work, and the special applicability of the salts to certain oxidation processes becomes more and more evident. In some respects, however, there seems to be misconception regarding the typical mode of action of these

<sup>74</sup> D. R.-P. 193722; *A.*, ii, 689.

<sup>75</sup> Coppadoro, *Gazzetta*, 1908, **38**, i, 489; *A.*, ii, 596.

<sup>76</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 1637; *A.*, ii, 1043.

compounds; although they are derivatives of hydrogen peroxide (from many points of view, some name, such as peroxydisulphonic acid, indicating this relation more clearly would be preferable to persulphuric acid), they do not in aqueous solution tend so much to give up oxygen directly as to take up metal; that is to say, the standard mode of decomposition is comparable to the second kind of action observable with hydrogen peroxide, as previously noted. This is well exemplified by the action of persulphates on metals, metallic halides, thiosulphates, lower salts of metals which form two basic oxides, etc., and is most conveniently expressed by the use of ionisation formulæ; in all such cases, the action is then merely the assumption of two extra negative charges by  $S_2O_8''$ , forming  $2SO_4''$ , for example,  $Zn + S_2O_8 = Zn^{++} + 2SO_4''$ ,  $2Br' + S_2O_8 = Br_2 + 2SO_4''$ ,  $2Fe^{++} + S_2O_8 = 2Fe^{+++} + 2SO_4''$ . In one at least of recent papers on the interaction between metals and persulphates,<sup>77</sup> there is a tendency to look upon the action as being in many cases an indirect one, through co-operation of water. It is true that not infrequently the final result is not just the simple one indicated above, but in these cases the cause is to be sought in subsequent secondary actions. When ammonium persulphate is the salt used, as is generally the case, the possibility of complications occurring is considerably greater than is the case with the potassium salt. It has been long known that persulphate oxidises ammonia and the ammonium radicle with production of nitrogen and of nitrate,<sup>78</sup> and therefore the action of the persulphate radicle itself on any particular substance is better observed by using the potassium salt. But even with this salt, complications may arise, due, for example, to hydrolysis of the primary product; an acid solution may be developed, resulting in hydrolysis of persulphuric acid and formation of hydrogen peroxide, which in its turn may be the source of the free oxygen which has sometimes been observed. The extent to which this latter hydrolysis may take place is evidenced by the fact that in a recent patent<sup>79</sup> this is claimed as a mode of preparing hydrogen peroxide, special conditions and precautions, of course, being necessary. In circumstances where this kind of action does not come into play, however, the reactions into which persulphates most readily enter are undoubtedly those which can be referred to the simple ionic change already mentioned.

One or two points concerning sulphur\* analogues of the class of

<sup>77</sup> M. G. Levi and others, *Gazzetta*, 1908, **38**, 583; *A.*, ii, 581. See also Turrentine, *J. Physical Chem.*, 1907, **11**, 623; *A.*, ii, 104.

<sup>78</sup> See also Levi and Migliorini, *Gazzetta*, 1908, **38**, ii, 10; *A.*, ii, 835; Kempf and Oehler, *Ber.*, 1908, **41**, 2576; *A.*, ii, 764.

D.R.-P. 199958; *A.*, ii, 1028.

substances dealt with in this section may also conveniently be referred to here.

From time to time conflicting statements have been made as to the true composition of "hydrogen persulphide." After first having been determined to be somewhat complex, it was later assumed to be represented by the formula  $\text{H}_2\text{S}_2$ , from analogy to hydrogen peroxide; then various higher sulphides were supposed to exist, corresponding with the polysulphides of the metals, but this was contradicted by Rebs,<sup>80</sup> who stated that whatever polysulphide might be added to an acid, the resulting hydrogen compounds were  $\text{H}_2\text{S}$  and  $\text{H}_2\text{S}_5$  only. This in turn is now shown to be incorrect, on the authority of independent investigators. By fractional distillation (under low pressure) of the oil obtained by pouring alkali polysulphide solution into hydrochloric acid, the disulphide,  $\text{H}_2\text{S}_2$ ,<sup>81</sup> and the trisulphide,  $\text{H}_2\text{S}_3$ ,<sup>82</sup> have been isolated as unstable liquids. The composition has been exactly determined by improved methods of analysis (the hydrogen being driven out as hydrogen sulphide, which could be accurately estimated), and the molecular weight by cryoscopic methods. Evidence is also published for the existence of compounds from  $\text{H}_2\text{S}_5$  to  $\text{H}_2\text{S}_9$ .<sup>83</sup> In discussing the constitution of these polysulphides, Bloch<sup>84</sup> is not unfavourable to Mendeléeff's conception of a possible "homologous series" formed from HSH by successive replacements of H by SH; the general formula for such a series would of course be  $\text{S}_n\text{H}_2$ .

In view of various investigations carried out in recent years, it has been suggested that tetrathionic acid has a peroxidic constitution,  $(\text{HO}_2\text{S}_2)\cdot\text{O}\cdot\text{O}\cdot(\text{S}_2\text{O}_2\text{H}_2)$ , and not the persulphidic constitution,  $(\text{HO}_3\text{S})\cdot\text{S}\cdot\text{S}\cdot(\text{SO}_3\text{H})$ , generally assumed, the reason being that alkaline reducing agents *apparently* abstract oxygen directly from its salts; thus, alkaline arsenite solution forms arsenate as well as monothioarsenate. It has been shown,<sup>85</sup> however, that there are serious objections to the assumption of a peroxide union in the tetrathionates, and that Mendeléeff's persulphide formula, which fits in so well with the general behaviour of the salts, can perfectly well account for these new facts also.

<sup>80</sup> *Annalen*, 1888, **246**, 356; *A.*, 1888, 1155.

<sup>81</sup> I. Bloch and F. Hohn, *Ber.*, 1908, **41**, 1961, 1975; *A.*, ii, 579.

<sup>82</sup> Bloch and Hohn, *ibid.*, 1971; *A.*, ii, 579. R. Schenck and V. Falcke, *ibid.*, 2600; *A.*, ii, 762.

<sup>83</sup> G. Bruni and A. Borgo, *Atti R. Accad. Lincei*, 1907, [v], **16**, ii, 745; *A.*, ii, 102.

<sup>84</sup> *Ber.*, 1908, **41**, 1980; *A.*, ii, 580.

<sup>85</sup> Price and D. F. Twiss, *Trans.*, 1907, **91**, 2021; J. E. Mackenzie and H. Marshall, *Trans.*, 1908, **93**, 1726.

*Complex Salts.*

Although a short section under the above heading seems in many ways desirable, it is a difficult matter to treat collectively the widely different substances which are thus brought together. In the absence of general guiding principles, also, any decision as to what are, and what are not, included under the term must appear very arbitrary and, in what follows, no attempt is made at any really systematic treatment.

In view of the great development which certain branches of the subject have now attained, the appearance of any collective account of any of these branches is to be welcomed. During the period under review the cobaltammine compounds have thus been treated by P. Pfeiffer,<sup>86</sup> and the fact that the description of these substances extends over 212 large pages gives some idea of the extent to which this field has been cultivated. The same author has tabulated the numerous cases of isomerism which have been observed amongst the complex chromium derivatives.<sup>87</sup> A. Colson, who has published many papers dealing with the green chromic sulphates, has recently given a collected statement of the results obtained by himself.<sup>88</sup> A class of complicated compounds which so far has not received a great deal of systematic investigation is the series of complex acids and salts derived from molybdenum trioxide and analogous substances; more attention is now being devoted to these, and a discussion of their probable constitution has been published by A. Miolati and R. Pizzighelli.<sup>89</sup>

The polyhalides of the alkali metals may fairly well be called complex salts; their probable constitution is certainly quite obscure. It is therefore highly desirable that there should be no doubt as to what members of the group actually exist, and at present the matter cannot be considered as settled. According to the most recent investigation,<sup>90</sup> the only iodine derivatives of the metals potassium, rubidium, and caesium which can be obtained at 25° are:  $KI_3$ ,  $RbI_3$ ,  $CsI_3$ ,  $CsI_5$ , and  $KI_7$ . The compounds,  $RbI_7$ ,  $RbI_9$ ,  $CsI_7$ ,  $CsI_9$ , mentioned by Abegg and Hamburger could not be obtained.

Complex halogen derivatives of two metals have come in for further examination in the case of several members of the platinum group. In the case of the iridium compounds, the iridi-salts ( $M_2IrCl_6$ ) present no novel characteristics, but the iridio-salts exhibit several features of interest from the point of view of Werner's theory of co-ordinated

<sup>86</sup> Gmelin-Kraut's *Handbuch der anorganischen Chemie*, Bd. V, Abt. 1.

<sup>87</sup> *Zeitsch. anorg. Chem.*, 1908, **58**, 317; *A.*, ii, 594.

<sup>88</sup> *Ann. Chim. Phys.*, 1907, [viii], **12**, 433; *A.*, ii, 45.

<sup>89</sup> *J. pr. Chem.*, 1908, [ii], **77**, 417; *A.*, ii, 595.

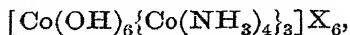
<sup>90</sup> H. W. Foote and W. C. Chalker, *Amer. Chem. J.*, 1908, **39**, 561; *A.* ii, 586.

compounds.<sup>91</sup> They can easily be prepared from the iridi-salts by reduction with normal oxalates. The salts are of two types, namely,  $M_3IrCl_6$  and  $M_2IrCl_5$ , the best example of the former being the sodium salt,  $Na_3IrCl_6 \cdot 12H_2O$ . The corresponding salts of the potassium metals and of ammonium readily change into those of the other type by the action of water; these contain a molecule of water, which is not driven off at  $150^\circ$ , and are therefore to be looked upon as *aquoiridio-pentachlorides*,  $M_2(H_2O, Cl_5Ir)$ . The hexachlorides are easily dehydrated.

A number of analogous derivatives of rhodium have been prepared and investigated in connexion with a search for material suitable for use in determinations of the atomic weight of that element.<sup>92</sup> These "rhodipentachlorides"<sup>93</sup> also fall into two classes similar to those mentioned above for iridium, and in the second class the molecule of water again plays an important part. The corresponding bromine compounds, however, all crystallise in the anhydrous form.

In a series of papers, A. Werner continues the discussion of the preparation and the constitution of various groups of complex cobalt-ammine compounds.<sup>94</sup> Amongst these are a series of violeo-salts of dichlorotetramminecobalt,  $[Cl_2Co(NH_3)_4]X$ , stereoisomerides of the praseo-salts formerly known; they form intensely blue crystals, and are presumably *cis*-compounds (1:2-constitution). To the red salts isolated from Vortmann's insoluble sulphate (which is a mixture of red and green salts), the constitution  $\left[ (NH_3)_4Co \cdot \overset{NH_2}{\underset{OH}{\text{C}}} \cdot Co(NH_3)_4 \right] X_4$

is assigned, the two cobalt atoms being apparently bound through inactive amino- and hydroxyl groups. The designation " $\mu$ -amino-" is proposed for the former type of union, and the name of *octammine- $\mu$ -amino-ol-dicobalt* salts is adopted for these compounds. A considerable number of them have been prepared. Another series of di-cobalt derivatives has also been elucidated, and is represented by the formula  $[(NH_3)_3Co:(OH)_3:Co(NH_3)_3]X_3$ ; these hexamminetrioldicobalt salts are isomeric with the dodecamminehexoltetracobalt salts,



and are red in colour. A new set of iodo-salts, obtained by Sand and Bökman, has been shown to be the iodopentamminecobalt series,  $[CoI(NH_3)_5]X_2$ ; these salts are green in colour.

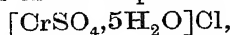
<sup>91</sup> M. Delépine, *Compt. rend.*, 1908, 146, 1267; *A.*, ii, 702.

<sup>92</sup> A. Gutbier and A. Hüttlinger, *Ber.*, 1908, 41, 210; *A.*, ii, 200.

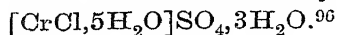
<sup>93</sup> There is room for the adoption of some more systematic nomenclature for substances of this kind; it seems unfortunate that whilst  $K_2IrCl_5$  is *potassium iridichloride*,  $K_2RhCl_5$  is *potassium rhodipentachloride*.

<sup>94</sup> *Ber.*, 1907, 40, 4605, 4817, 4834; 1908, 41, 3007; also J. Sand and G. Bokman, *Abh.*, 40, 4497; *A.*, ii, 42, 43, 45, 950.

Physiochemical investigations regarding the hydrolysis and the molecular weight of the different chlorides and sulphates of chromium, with a view to the further elucidation of their constitution, have been carried out by various chemists.<sup>95</sup> The results do not seem to give concordant indications as to the molecular complexity of the green and blue varieties. A green chlorosulphate of chromium,



has been prepared, isomeric with that formerly known,



As indicated by the formulæ, the new salt easily gives Cl ions in solution, but not  $\text{SO}_4$  ions, just the opposite of what is the case with the other salt.

Complex salts, in which iron forms the central constituent, have been dealt with by several workers. New pyrophosphate derivatives are described,<sup>97</sup> some related to ferric oxide, some to ferrous; the best-defined of these are the ferric ones of the type  $\text{M}_6\text{Fe}_2(\text{P}_2\text{O}_7)_3$ , and crystallise with varying proportions of water; the acid itself has also been isolated. The analogy to the ferricyanides is pointed out ( $\text{P}_2\text{O}_7$  equivalent to  $4\text{CN}$ ), and it is proposed to call the salts ferripyrophosphates; the ferropyrophosphates,  $\text{M}_4\text{Fe}_2(\text{P}_2\text{O}_7)_3$ , are powerful reducing agents (see p. 58). Analogous salts derived from metals other than iron have also been prepared.

There has been a good deal of further investigation of the ferro-nitrosulphides (Roussin's salts) referred to in last year's Report (p. 71<sup>98</sup>), in the hope of clearing up their constitution, and several co-ordination formulæ are suggested for the two classes of compounds. When the salts are decomposed in various ways, the nitrogen is obtained in different stages of oxidation—nitrous or nitric oxide, hyponitrite, nitrite—according to the circumstances.<sup>99</sup>

Many of the complex salts derived from molybdenum and tungsten contain twelve atoms of the respective element in the molecule. In the paper by Mioletti and Pizzighelli, already mentioned, it is suggested that the acids may all be represented by co-ordination formulæ of the type  $[\text{R}(\text{Mo}_2\text{O}_7)_6]\text{H}_n$ , where  $n$  is 7 if R represents an element like phosphorus, and 8 when R is an element like silicon. The formulæ stated by various other investigators for substances prepared by them do not, however, correspond with acids of this basicity.

<sup>95</sup> J. Sand and F. Grammling, *Zeitsch. physikal. Chem.*, 1908, **62**, 1, 28; H. G. Denham, *Zeitsch. anorg. Chem.*, 1908, **57**, 361; *A.*, ii, 293, 294, 389.

<sup>96</sup> R. F. Weinland and T. Schumann, *Zeitsch. anorg. Chem.*, 1908, **58**, 176; *A.*, ii, 595.

<sup>97</sup> P. Pascal, *Compt. rend.*, 1908, **146**, 231; *A.*, ii, 193.

<sup>98</sup> The formula  $\text{HFe}_4(\text{NO})_7\text{S}_3$  is there printed incorrectly.

<sup>99</sup> L. Cambi; I. Bellucci and P. de Cesaris, *Atti R. Accad. Lincei*, 1907, [v], **16**, ii, 658, 740; 1908, [v], **17**, i, 202, 424, 545; *A.*, ii, 41, 111, 288, 499, 593.

Mercuric cyanide reacts with a number of other mercuric salts (for example, the perchlorate) to form complex derivatives; from a physico-chemical study of the properties of the solutions of these compounds,<sup>1</sup> proof is obtained that the mercury in them forms part of a complex univalent cation,  $(\text{HgCN})^+$ . A number of the salts have been prepared in the crystalline condition; their dilute solutions give no precipitate on the addition of sodium hydroxide. Even the compound of mercuric cyanide with mercuric oxide appears to be the basic oxide,  $(\text{HgCN})_2\text{O}$ , and to give a hydroxide,  $(\text{HgCN})\text{OH}$ , when it dissolves in water. Similar complex cations apparently are formed from mercuric perchlorate and mercuric iodide, bromide, and chloride, the tendency to form them decreasing in the order given. Crystalline compounds are obtainable in the first and second case, but not in the last; these compounds are decomposed by treatment with water.

### *Colloids.*

During recent years much interesting work has been done in connexion with colloids generally, and a considerable proportion of the new developments have to deal with the inorganic branch of the subject. Many of the papers which have appeared in the course of the past year fall rather within the domain of physical chemistry, but others of a more descriptive character may be referred to here.

Colloidal sulphur has already been prepared by the method of using electrical discharges; it is now shown<sup>2</sup> that it can also be obtained from the sulphur which separates when sodium thiosulphate solution is added to cold concentrated sulphuric acid. The liquid is somewhat diluted, heated, filtered through glass wool, and allowed to cool; these processes are repeated so long as any sulphur, which will not redissolve, is precipitated. A cloudy, yellowish-coloured mass is thus obtained, which, on warming, forms a liquid, which is apparently perfectly clear; it separates again on cooling. This mass is separated as completely as possible by means of a centrifuge, and is partly washed in a similar manner, after which the remaining acid is neutralised with sodium carbonate. The product is soluble in water, but if the attempt is made to remove the sodium sulphate from the hydrosol by dialysis, insoluble sulphur is very soon deposited. Dilute solutions, in which the sulphuric acid has not been neutralised, can be preserved for a long time, but the hydrosol very easily precipitates insoluble sulphur on addition of various salts.

The preparation of a more or less colloidal form of graphite, specially suitable for lubricating purposes, has been effected by prolonged

<sup>1</sup> V. Borelli, *Gazzetta*, 1908, **38**, i, 261; ii, 421; *A.*, i, 515; ii, 1039.

<sup>2</sup> M. Raffo, *Zeitsch. Chem. Ind. Kolloide*, 1908, **2**, 358; *A.*, ii, 683.



agitation of the graphite with a solution of tannic acid;<sup>3</sup> the material thus obtained passes through filters and remains in suspension for months, but it becomes flocculated on the addition of hydrochloric acid. The method of preparation was based on the known action of tannic acid and other substances on china-clay, by which the latter is rendered much more workable for certain pottery purposes; a fluid "slip," suitable for casting in forms, can by such means be prepared with much less water than formerly had to be used.

Convenient reducing agents for the preparation of colloidal metals and some other reduction products are found to be provided by the ferropyrphosphates of the alkali metals<sup>4</sup>—salts which can be easily prepared in solution by adding a solution of ferrous salt to a solution of an ordinary alkali pyrophosphate. (Solutions of these and similar complex pyrophosphates are useful also in connexion with the electro-deposition of certain metals for purposes of quantitative analysis.) The colloidal solutions of gold and silver obtained in this way are of a very intense colour, and it is stated that the reaction may be used as a colorimetric method of estimating these metals. Strange to say, platinum compounds give no result with this reagent, but cupric and mercuric salts can be reduced first to the lower stage of oxidation and then to colloidal metals. The colloidal cuprous hydroxide, which can be obtained in this way, appears yellow by reflected light, and is said to provide a very sensitive reaction in testing for traces of copper.

In the state of colloidal solution, palladium still exhibits the property of absorbing hydrogen,<sup>5</sup> forming a hydrosol of the "hydride"; and in this state its power of absorption is much greater than is the case when it is in the form of palladium black. This absorbs, at most, somewhat less than nine hundred times its volume of the gas, but the colloidal form takes up from nine hundred to nearly three thousand times its volume. (No explanation can be given for the great fluctuations of the value found in different experiments.) The colloidal hydride reacts rapidly with any free or loosely-combined oxygen which may be present, and the numbers given have been corrected for the hydrogen used up in this way.

The bearing which colloidal silver and silver compounds have in relation to photographic images, and to the photo-chemistry of silver generally, is discussed in a series of papers by Lüpke-Cramer;<sup>6</sup> he considers that the "sub-halides" of silver are not definite compounds, but adsorption products, and that the different appearances of the

<sup>3</sup> E. G. Acheson, *J. Franklin Inst.*, 1907, **164**, 375; *A.*, ii, 375.

<sup>4</sup> P. Pascal, *Compt. rend.*, 1908, **146**, 862; *A.*, ii, 500.

<sup>5</sup> C. Paal and J. Gerum, *Ber.*, 1908, **41**, 805; *A.*, ii, 392.

<sup>6</sup> *Zeitsch. Chem. Ind. Kolloide*, 1907, **2**, 135; 1908, **2**, 360; **3**, 33, 135; *A.*, ii, 378, 691, 841, 945.

silver images obtained with different developers are due to the more or less colloidal state of the silver and the different substances adsorbed by it from the developer. (The other view receives favourable consideration from Trivelli,<sup>7</sup> who gives a full discussion of both theories.)

A specially interesting development in the study of colloids recently has been the preparation in colloidal form of a number of what were formerly considered the very antitheses of such substances—the typical “crystalloid” salts, such as the halides of the alkali metals; organosols of these can be obtained by the interaction of suitable compounds, such as ethyl ethylsodiummalonate and ethyl chloroacetate,<sup>8</sup> dissolved in anhydrous ether, benzene, etc. Similar results have also been obtained with a number of salts of magnesium and the metals of the alkaline earths; it appears more and more likely, therefore, that substances generally may be obtained in the colloidal form if only they can be produced by interactions in solvents in which the solubility of the ordinary form of the product is sufficiently slight. Colloidal barium sulphate<sup>9</sup> can be obtained by double decomposition in glycerol solutions of the reacting salts; the hydrosol thus obtained is particularly stable in presence of barium nitrate, although salts of most other metals precipitate it; it is also coagulated by polybasic acids, but not by monobasic. A newly-devised general method for obtaining colloidal salts of the metals of the alkalis and the alkaline earths consists in acting with the appropriate acid on the thiocyanate of the metal, each substance being dissolved in a mixture of ether and amyl alcohol.<sup>10</sup> A number of colloidal salts of magnesium and the metals of the alkaline earths can also be prepared by the interaction of the appropriate acid on the basic oxide of the metal, dissolved in methyl alcohol.<sup>11</sup>

In general, the various salts prepared by these methods can be precipitated, as gels, by the addition of suitable liquids, and re-dissolved in the colloidal form, by means of others which act as appropriate “solvents.”

Some interesting experiments which had for their aim the preparation of gelatinous aluminium silicates, of definite composition, by the interaction of sodium silicate and aluminium acetate, gave entirely negative results;<sup>12</sup> from their behaviour towards solvents, etc., the precipitates obtained in this way appear to be merely mechanical

<sup>7</sup> *Zeitsch. wiss. Photograph. Photophysik. Photochem.*, 1908, **6**, 358; *A.*, ii, 1036.

<sup>8</sup> C. Paal and G. Kuhn, *Ber.*, 1908, **41**, 51, 58; *A.*, ii, 179.

<sup>9</sup> A. Recoura, *Compt. rend.*, 1908, **146**, 1274; *A.*, ii, 692.

<sup>10</sup> P. P. von Weimarn, *Zeitsch. Chem. Ind. Kolloide*, 1908, **3**, 89; *A.*, ii, 842.

<sup>11</sup> C. Neuberg and B. Rewald, *Sitzungsber. K. Akad. Wiss. Berlin*, 1907, 820; *A.*, ii, 39; *Biochem. Zeitsch.*, 1908, **9**, 537; *A.*, ii, 495.

<sup>12</sup> H. Stremme, *Centr. Min.*, 1908, 622, 661; *A.*, ii, 1041.

mixtures of hydrated alumina and hydrated silica. This observation, taken in conjunction with the widely variable composition of the natural non-crystalline and clay-like substances known as halloysite, allophane, etc., leads to the conclusion that these are not definite compounds, but variable mixtures.

### *Rare Earths.*

As in former years, there has again been a considerable amount of investigation carried out in connexion with this complicated group of substances, but there is not much of it that calls for special comment in a general résumé; the most noteworthy result, the separation of ytterbium into two components, has already been mentioned (p. 34). The search for improved means of fractionation, of course, continues, and several new or modified processes are suggested. Amongst the salts recommended for the purpose are the bromates;<sup>13</sup> starting from the oxalates, they are obtained by treatment with sulphuric acid, followed by double decomposition with barium bromate. Other compounds which have proved serviceable for certain groups of elements are the malonates, obtained directly from the hydroxides by the action of malonic acid, and the 1-naphthol-8-sulphonates,<sup>14</sup> obtained from the carbonates by the action of the sulphonic acid; the solubilities of many of the salts of these acids have been definitely measured.

A considerable number of new compounds of the rare-earth metals have been prepared and described, but generally they exhibit no striking or exceptional characters. Several sulphides have been examined,<sup>15</sup> and some of these have been found to give a distinct odour of hydrogen persulphide when acted on by hydrochloric acid; it is therefore suggested that, say, cerium disulphide is not a simple sulphide,  $\text{Ce} \begin{smallmatrix} \text{S} \\ \text{S} \end{smallmatrix}$ , but a persulphide, and might be written  $\text{Ce}_2\text{S}_3\text{S}$ . Several substances, partly oxide and partly sulphide, have also been obtained.

### *The Argon Group.*

The most interesting contribution to our knowledge of this class of elements which has been made during the year has undoubtedly been the liquefaction of helium by Onnes,<sup>16</sup> regarding which a communication was also made to the Chemistry Section of the British Association at Dublin by Sir James Dewar. Premature announcements of success

<sup>13</sup> C. James, *Chem. News*, 1908, 97, 61, 205; *A.*, ii, 190, 498.

<sup>14</sup> H. Erdmann and F. Wirth, *Annalen*, 1908, 361, 190; *A.*, i, 621; ii, 694.

<sup>15</sup> A. Duboin, *Compt. rend.*, 1908, 146, 815; *A.*, ii, 502; W. Biltz, *Ber.*, 1908, 41, 3341; *A.*, ii, 1037.

<sup>16</sup> *Proc. K. Akad. Wetensch. Amsterdam*, 1908, 10, 744; 11, 168; *A.*, ii, 490, 944.

had been made, but it was found that the results on which these were based had been obtained with impure material, and that one milligram of hydrogen, diffused through a space of 7 c.c., brought about peculiar phenomena in the highly compressed and cooled helium, which had caused it to be assumed that liquefaction of this element had taken place.

For the thorough purification of the material—two hundred litres of helium were used for the final condensation—Dewar's method of absorption in charcoal at low temperatures was employed in conjunction with the usual chemical methods for eliminating active elements. Preliminary study of the isotherms for helium at the temperatures producible by liquid hydrogen had shown that the Joule-Kelvin effect would probably be sufficient to secure condensation, so that the Linde-Hampson method of working should prove successful, and the apparatus by which the result was actually obtained was similar to that used for the liquefaction of hydrogen. Considerable quantities of liquid air and hydrogen for auxiliary cooling were prepared beforehand, and three hours' work on the helium sufficed to produce fully 60 c.c. of colourless, transparent liquid, having a density of only 0.15. It boils at  $4.5^{\circ}$  Abs., which is within one degree of its critical point; attempts to freeze it by rapid evaporation under diminished pressure were unsuccessful, although the temperature reached was probably about  $3^{\circ}$  Abs.

Attempts have been made to obtain compounds of argon by means of arc and spark discharges in liquid argon, using electrodes of various metals, but without success.<sup>17</sup> A polymerisation of the element could not be expected from a monatomic gas (the formation of ozone by similar processes presumably depends on the preliminary rupture of the diatomic molecule). Apparently there is no tendency to form even unstable compounds with the material of the electrodes; such compounds, if formed at the temperature of the discharge, might possibly become fixed by the very rapid cooling.

Most of the other work of the year deals almost entirely with the natural occurrence of the various gases, and with unsuccessful attempts to discover other members of the group. It would now appear to be fairly certain that no other gases are present in the atmosphere in appreciable quantity; the residues from about 120 tons of liquid air have been subjected to a searching examination,<sup>18</sup> but no indications of any unknown element could be obtained; other experiments have also given negative results. It has been suggested by Sir William Ramsay that the emanation from the radioactive elements may represent the higher members of this group.

<sup>17</sup> F. Fischer and G. Ilievici, *Ber.*, 1908, **41**, 3802; *A.*, ii, 1034.

R. B. Moore, *Proc. Roy. Soc.*, 1908, **81**, A, 195; *A.*, ii, 840.

Some very striking figures regarding the total quantity of noble gases evolved from certain thermal springs are given by C. Moureu and R. Biquard ;<sup>19</sup> according to their results, one spring, the Bourbon-Lancy, must evolve in the course of a year fully sixteen thousand litres of noble gases, of which quantity no less than ten thousand litres consist of helium. All the waters of these springs are radioactive, a point of considerable interest in connexion with the production of helium from radium emanation.

### *Group I.*

As was mentioned in last year's Report (p. 47), calcium hydride has been suggested as a convenient and portable material for use in the preparation of hydrogen, which is obtained merely by the action of water on it ; a competitor now appears in the form of aluminium filings which have been treated with small quantities of potassium cyanide and mercuric chloride.<sup>20</sup> The hydrogen is obtained by dropping water on the prepared metal, and the action takes place rapidly if the supply of water is so regulated as to permit of the temperature being maintained at 70° by the heat evolved in the action. One gram gives about 1·3 litres of gas at the ordinary temperature, as compared with about 1 litre in the case of calcium hydride.<sup>21</sup>

The possible utilisation of natural silicates as sources of potassium compounds on the large scale has been investigated ; although potash-felspar when finely divided may be decomposed by water or aqueous solutions of various salts, the methods so far tried do not promise to be sufficiently economical to be practicable.<sup>22</sup> Leucite, which is also richer in potassium, can be fairly easily decomposed by sulphuric acid or nitric acid, and various processes for separating potassium salts from the solutions thus prepared are suggested.<sup>23</sup>

The relative solubilities of metallic silver in molten lead and zinc, which are so widely different that the desilverisation of lead by zinc (Parkes' process) is the best method known, have been determined at various concentrations.<sup>24</sup> At 500° the partition coefficient Zn : Pb is about 300 : 1. In Parkes' process the separation is effected at a much lower temperature than this, the zinc being allowed to solidify, and under these conditions this ratio is increased greatly in favour of the zinc.

<sup>19</sup> *Compt. rend.*, 1908, **146**, 435 ; *A.*, ii, 277.

<sup>20</sup> Maurichoau-Beaupré, *ibid.*, 1908, **147**, 310 ; *A.*, ii, 829.

<sup>21</sup> In last year's Report, the volume of hydrogen stated is only one-tenth of the correct amount.

<sup>22</sup> A. S. Cushman and P. Hubbard, *J. Amer. Chem. Soc.*, 1908, **30**, 779 ; *A.*, ii, 586.

<sup>23</sup> C. Manuelli, *Gazzetta*, 1908, **38**, i, 143 ; *A.*, ii, 386.

\* <sup>24</sup> G. N. Potdar, *J. Coll. Sci. Tōkyō*, 1908, **25**, ix, 1 ; *A.*, ii, 945.

Finely-divided gold is energetically attacked by fused sodium peroxide, with formation of sodium aurate, and from this salt, by means of dilute sulphuric acid, auric acid,  $\text{H}_3\text{AuO}_3$ , or, more probably,  $\text{HAuO}_2, \text{H}_2\text{O}$ , can be obtained. To prepare aurates satisfactorily from the acid, it should be treated with the pure appropriate hydroxide in an atmosphere free from carbon dioxide, and the resulting solution should then be evaporated in the dark.<sup>25</sup>

### Group II.

The properties of metallic calcium and its capabilities as a chemical reagent continue to receive a fair amount of attention, and several papers dealing with various reactions in which it takes part have recently appeared. These include an investigation of its action on ammonia and on amino-derivatives under various conditions; <sup>26</sup> it is particularly reactive with arylamines, producing compounds of the type  $(\text{NHR})_2\text{Ca}$ . Further information regarding the use of the metal and its hydride as reducing agents in "thermite" processes has also been published, <sup>27</sup> reactions with the hydride are less violent than with the free metal.

Within the last few years an extensive series of investigations has been carried out on the compounds formed by union of calcium sulphate and other metallic sulphates, and a considerable number of new salts have been obtained; during the year this work has been continued, and additional double and triple sulphates, such as  $\text{Rb}_2\text{Ca}_2(\text{SO}_4)_3$  and  $\text{K}_2\text{Ca}_2\text{Cd}(\text{SO}_4)_2, 2\text{H}_2\text{O}$ , have been prepared.<sup>28</sup> When water of crystallisation is not taken into account, salts of this kind are easily enough represented by ordinary constitutional formulæ. Anhydrous calcium sulphate (the mineral *anhydrite*) is frequently treated as being isomorphous with the sulphates of strontium, barium, and lead; like them it forms rhombic crystals, but its axial ratios differ considerably from those of the other sulphates; it is now shown fairly conclusively that it is not isomorphous with these. The various salts have been prepared artificially in crystals of moderate size by deposition from solution in hot concentrated sulphuric acid, and it is found that calcium sulphate does not form mixed crystals with the others, which, however, form mixed crystals among themselves.<sup>29</sup>

<sup>25</sup> F. Meyer, *Compt. rend.*, 1907, **145**, 805; *A.*, ii, 47.

<sup>26</sup> H. Erdmann and H. van der Smissen, *Annalen*, 1908, **361** 32; *A.*, ii, 587.

<sup>27</sup> F. M. Perkin and L. Pratt, *Trans. Faraday Soc.*, 1908, **3**, 179; *A.*, ii, 379.

<sup>28</sup> J. D'Aus, *Ber.*, 1907, **40**, 4912; 1908, **41**, 187, 1776, 1777; *A.*, ii, 104, 182, 890.

P. Gaubert, *Compt. rend.*, 1907, **145**, 877; *A.*, ii, 38.

It would appear that bicarbonates of this group of metals can really exist in the solid state, although they are exceedingly unstable;<sup>30</sup> thus, when ammonium or potassium bicarbonate solution is added to a solution of calcium chloride, both being cooled to zero, a white, crystalline precipitate is obtained, the composition of which approximates to that expressed by the formula  $\text{Ca}(\text{HCO}_3)_2$ .

An interesting description is given of the working up of the residues from 30,000 kilograms of pitchblende residues for radium.<sup>31</sup> The operations extended over two years, and the total radium contained in the products was equivalent to rather more than 3 grams of radium chloride. A final fraction of radium bromide was found to lose bromine on keeping. An atomic weight determination on the chloride gave the value  $\text{Ra} = 225$ .

### Group III.

There has been comparatively little work done in connexion with this group, beyond that dealing with "thermite" reactions and the preparation of alloy-like derivatives of boron and silicon. Indium selenate has been prepared, and its ability to form alums demonstrated by the isolation of the caesium salt,  $\text{CsIn}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ , in octahedral crystals.<sup>32</sup> A number of crystallised complex silico-tungstates containing indium have also been described, analogous to similar compounds formed by aluminium, iron, chromium, etc.<sup>33</sup>

### Group IV.

The absorption of carbon monoxide by solutions of cuprous chloride and other salts has been investigated on somewhat similar lines to those referred to in last year's Report (p. 57) with regard to nitric oxide and various metallic salts.<sup>34</sup> The proportion of gas absorbed never exceeds the ratio  $\text{CO} : \text{Cu}$ , and in all kinds of aqueous solutions a definite compound,  $\text{CuCl} \cdot \text{CO} \cdot 2\text{H}_2\text{O}$ , is formed with the chloride. No absorption takes place except in the presence of water, ammonia, aniline, or other substance capable of forming additive compounds like that above formulated.

In addition to a fair amount of work on the preparation of silicides and silicon alloys, and on "thermite" processes involving silicon,

<sup>30</sup> E. H. Keiser and others, *J. Amer. Chem. Soc.*, 1908, **30**, 1711, 1714; *A.*, ii, 1036, 1037.

<sup>31</sup> L. Haitinger and K. Ulrich, *Monatsh.*, 1908, **29**, 486; *A.*, ii, 857.

<sup>32</sup> F. C. Mathers and C. G. Schluederberg, *J. Amer. Chem. Soc.*, 1908, **30**, 211; *A.*, ii, 386.

<sup>33</sup> G. N. Wyrouboff, *Bull. Soc. franç. Min.*, 1907, **3**, 277; *A.*, ii, 386.

<sup>34</sup> W. Manchot and J. N. Friend, *Annalen*, 1908, **359**, 100; *A.*, ii, 375.

there has been a good deal of investigation as to the formation of silicic acids and soluble silicates. As a result, there appears to be very considerable doubt as to the existence of any definite hydrate of silica whatsoever.<sup>35</sup> From a determination of the amount of hydrogen evolved when certain silicides and titanides are decomposed by such agents as hydrofluoric acid, sulphuric acid, or potassium hydroxide, W. Manchot<sup>36</sup> seeks to show that in compounds of that class silicon and titanium form chains, but the evidence does not seem to justify the construction of constitutional formulæ for such substances.

Pure zirconium fluoride, which can be easily prepared by the action of dry hydrogen fluoride on zirconium chloride, forms a snow-white, crystalline powder, which, as regards chemical character, is surprisingly inert.<sup>37</sup> It is sparingly soluble in water, and does not undergo hydrolysis, but can be re-precipitated as a hydrate,  $\text{ZrF}_4 \cdot 3\text{H}_2\text{O}$ .

#### Group V.

A very large amount of work in connexion with the members of this group has recently appeared. A considerable proportion of the interest centres around problems connected with the technical utilisation of atmospheric nitrogen, either by oxidation to nitrite and nitrate or by reduction to ammonia.

A number of metallic nitrides have been studied, their preparation being effected by heating the metals in an atmosphere either of nitrogen<sup>38</sup> or of ammonia.<sup>39</sup> The temperatures at which metals absorb nitrogen vary greatly in different cases: with magnesium, calcium, aluminium, and chromium the process begins at about  $800^\circ$ , but with iron, copper, and some others no action occurs below  $1250^\circ$ . In the first three cases, definite compounds are formed, namely,  $\text{Mg}_3\text{N}_2$ ,  $\text{Ca}_3\text{N}_2$ , and  $\text{AlN}$ ; in the other cases the proportion of nitrogen absorbed is not sufficient to form compounds of this "ammonia type," and it is doubtful whether the resulting substance is not of the nature of a solid solution, of nitrogen or metallic nitride, in the metal. An interesting character of several of these products is that they are magnetic; in some (chromium and titanium) this property is distinctly noticeable, and in the case of manganese (12 per cent. nitrogen) it is almost as intense as in the case of iron. It varies greatly with the composition, however, and attains a maximum

<sup>35</sup> O. Mugge, *Centr. Min.*, 1908, 129; J. M. van Bemmelen, *Zeitsch. anorg. Chem.*, 1908, 59, 225; H. Le Chatelier, *Compt. rend.*, 1908, 147, 660; *A.*, ii, 277, 838, 1033.

<sup>36</sup> *Annalen*, 1907, 357, 129, 140; *A.*, ii, 40, 46.

<sup>37</sup> L. Wolter, *Chem. Zeit.*, 1908, 32, 606; *A.*, ii, 701.

<sup>38</sup> I. I. Shukoff, *J. Russ. Phys. Chem. Soc.*, 1908, 40, 457; *A.*, ii, 484.

<sup>39</sup> G. G. Henderson and J. C. Galletly, *J. Soc. Chem. Ind.*, 1908, 27, 387; *A.*, ii, 485.



according to other observers<sup>40</sup> at a composition which would correspond with the formula  $Mn_7N_2$ . When metals are heated in ammonia instead of nitrogen, the results obtained are somewhat similar; in cases where no distinct fixation of nitrogen takes place (for example, tin), there is nevertheless a considerable change in the physical condition of the metal, and a considerable proportion of the ammonia undergoes decomposition into its elements.

The formation of definite compounds when metals dissolve in liquid ammonia, assumed by Moissan and others, is denied by Kraus<sup>41</sup> so far as lithium, sodium, and potassium are concerned, but confirmed in the case of calcium; the compound is not represented by the formula  $Ca(NH_3)_4$ , however, as given by Moissan, but by  $Ca(NH_3)_6$ .

The direct formation of hydrazine from ammonia can be brought about, with a good yield, by means of sodium hypochlorite,<sup>42</sup> provided the viscosity of the solution has been increased by the addition of a small quantity of some suitable organic substance, such as glue. The further condensation of hydrazine to azoimide (hydrazoic acid) by means of oxidising agents is well known; oxidation by means of nitric acid forms a simple lecture experiment. A quantitative study of the behaviour of several allied oxidising agents under certain conditions has disclosed several peculiar results.<sup>43</sup> In presence of sulphuric acid, potassium chlorate gives a large yield of azoimide, bromate gives much less, and iodate gives none at all; in presence of silver sulphate, as well as sulphuric acid, all three give about the same yield (averaging about 12 per cent.), which is, however, much less than that obtained with chlorate in absence of silver (more than 22 per cent.). The actions with the halogens themselves also exhibit peculiarities. A convenient method for the actual preparation of azoimide is suggested<sup>44</sup> in the interaction of ethyl nitrite and hydrazine salts under certain conditions; thus, a yield of more than 80 per cent. can be obtained by shaking the ester for six hours with an aqueous solution of hydrazine sulphate and sodium hydroxide.

Ebler and Schott publish a long paper<sup>45</sup> dealing with hydroxylamine and its derivatives, in which they give a full discussion of its probable constitution; they accept the view that it is tautomeric, towards alkalis acting as a weak acid,  $NH_2 \cdot OH$ , and with acids acting as a weak base,  $NH_3 \cdot O$ , forming oxonium salts,  $NH_3 \cdot O < \begin{smallmatrix} H \\ X \end{smallmatrix}$ . Certain

<sup>40</sup> E. Wedekind and T. Veit, *Ber.*, 1908, **41**, 3769; *A.*, ii, 1041.

<sup>41</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 653; *A.*, ii, 486.

<sup>42</sup> F. Raschig, D.R.-P. 198307; *A.*, ii, 1029.

<sup>43</sup> A. W. Browne and F. F. Shetterly, *J. Amer. Chem. Soc.*, 1908, **30**, 53; *A.*, ii, 373.

<sup>44</sup> J. Thiele, *Ber.*, 1908, **41**, 2681; *A.*, ii, 940.

<sup>45</sup> *J. pr. Chem.*, 1908, [ii], **78**, 289; *A.*, ii, 1029.

metals, such as zinc and calcium, can displace hydrogen from it directly, forming more or less unstable *hydroxylamates*, for example,  $\text{Ca}(\text{O}\cdot\text{NH}_2)$ . It is also stated that hydroxylamine reacts like hydrogen peroxide with titanium solutions, giving the same yellow colour.

In connexion with the oxides of nitrogen, much of the recent work bears on the synthetic production of these substances at high temperatures, attained electrically or otherwise; a considerable proportion of this deals with the various equilibria which are established during the formation of the oxides<sup>46</sup> or during their absorption by water and solutions,<sup>47</sup> and cannot be entered upon here. Under suitable conditions, oxidation of the nitrogen may proceed as far as nitric anhydride (for example, nitrogen peroxide is rapidly oxidised into this by ozone), and in such a case synthetic nitric acid of high concentration may be prepared directly. The direct production of pure nitrites is another problem of great technical importance, and it is claimed that this result can be attained by oxidising atmospheric nitrogen to the appropriate extent in the electric arc, and maintaining the gases at a temperature not below  $300^\circ$  until absorption in solution of alkali hydroxide has been effected; in this way the formation of higher oxides is almost entirely prevented.<sup>48</sup> The analysis of mixtures of nitrogen oxides can be effected by examination of their ultra-red absorption spectra;<sup>49</sup> all five oxides, and also ozone, can be detected by their different maxima of absorption. In this way the nature of the products obtained under various conditions of electrical discharge, etc., can be conveniently examined.

Some interesting observations on the glowing of phosphorus and some of its compounds have been described. The glowing of phosphorous anhydride when mixed with oxygen has been investigated by Scharff,<sup>50</sup> who finds that it is influenced by temperature, oxygen-concentration, presence of other substances, etc., in very much the same way as is the glowing of phosphorus itself; to a certain extent this is also the case with the glowing of the sulphide  $\text{P}_2\text{S}_3$ . These results seem to point to the conclusion that the phosphorescence associated with the slow oxidation of phosphorus is due, not to the primary oxidation of the element, but to the subsequent oxidation of the phosphorous anhydride so produced. This view seems to be sup-

<sup>46</sup> E. H. Keiser and L. McMaster, *Amer. Chem. J.*, 1908, **39**, 101; *A.*, ii, 223. F. Haber and A. Koenig, *Zeitsch. Elektrochem.*, 1907, **13**, 725; **14**, 689; *A.*, ii, 34, 940.

<sup>47</sup> F. Foerster and M. Koch, *Zeitsch. angew. Chem.*, 1908, **21**, 2161, 2209; *A.*, ii, 941, 1031.

<sup>48</sup> Badische Anilin- & Soda-Fabrik, D.R.-P. 188188; *A.*, ii, 175.

<sup>49</sup> E. Warburg and G. Leithauser, *Sitzungsber. K. Akad. Wiss. Berlin*, 1908, 148; *A.*, ii, 175.

<sup>50</sup> *Zeitsch. physikal. Chem.*, 1908, **62**, 179; *A.*, ii, 373.

ported by a striking phenomenon observed by L. and E. Bloch<sup>51</sup> during an investigation of the ionisation effects which are produced when air is passed over phosphorus. They found that if the speed of the air current is increased, then the phosphorescence is drawn out in the direction of the current, and, on further increasing the speed, it becomes completely detached from the phosphorus; with a sufficiently long tube and suitably regulated current, a steady phosphorescent column may be obtained, separated from the phosphorus by a dark region several metres in length. In this dark space there is neither production of ozone nor ionisation, so that all three phenomena are directly connected. It is possible, of course, that the phosphorescence is due to phosphorus vapour which is carried forward, but more probably it is due to vapour of the oxide.

Several corrections of what are said to be erroneous statements regarding phosphorus compounds may be noted. Only three definite sulphides of phosphorus exist, namely,  $P_4S_3$ ,  $P_4S_7$ , and  $P_2S_5$ ,<sup>52</sup> other so-called sulphides being merely mixtures. The various "polyphosphates" are merely mixtures of pyrophosphate and metaphosphate.<sup>53</sup> Hypophosphoric acid corresponds with the simple formula  $H_2PO_3$ , as is shown by the molecular weights of its esters,<sup>54</sup> determined ebullioscopically on solutions in alkyl iodides.

A number of papers dealing with the subject of arsine have recently appeared, and yield a considerable amount of detailed information regarding its decomposition by heat,<sup>55</sup> its behaviour with solutions of various metallic salts,<sup>56</sup> and its oxidation.<sup>57</sup> With silver nitrate solution there is a certain amount of precipitation of silver arsenide,  $Ag_3As$ , and not of metallic silver alone, as is frequently stated; with ammoniacal nitrate solution, arsenide is also precipitated, but undergoes oxidation with formation both of arsenite and arsenate, and deposition of silver.

An interesting method of purifying, say, concentrated sulphuric acid from arsenic compounds has been patented;<sup>58</sup> it consists in converting the arsenic into chloride or fluoride by addition of the appropriate acid, and then extracting with benzene, which completely removes the arsenious halide; the benzene in turn can be purified by agitation with water. Dichlorobenzene acts in the same way, and can be applied in

<sup>51</sup> *Compt. rend.*, 1908, 147, 842; *A.*, ii, 1032.

<sup>52</sup> A. Stock, *Ber.*, 1908, 41, 558, 657; *A.*, ii, 274.

<sup>53</sup> N. Parravano and G. Calcagni, *Atti R. Accad. Lincei*, 1908, [v], 17, 1, 731; *A.*, ii, 838.

<sup>54</sup> A. Rosenheim and M. Pritze, *Ber.*, 1908, 41, 2708; *A.*, ii, 942.

<sup>55</sup> A. Stock and others, *Ber.*, 41, 1819; *A.*, ii, 488.

<sup>56</sup> H. Reckleben and others, *Zeitsch. anal. Chem.*, 1907, 46, 671; *A.*, ii, 36.

<sup>57</sup> H. Reckleben, *ibid.*, 1908, 47, 105; *A.*, ii, 176.

<sup>58</sup> Chemische Fabrik Griesheim-Elektron, D.R.-P. 194864; *A.*, ii, 686.

connexion with a scrubbing process for gases contaminated with arsenic ; in such cases its lower volatility is an advantage.

The rarer members of this group have recently received a considerable share of attention, and a large number of new compounds of them are described, many of them being of a complex kind. They include derivatives of so-called hypovanadic acid,  $V_2O_4 \cdot 2H_2O$ ,<sup>59</sup> which in these compounds exhibits basic functions ; whilst most of its derivatives are more or less decidedly blue in colour, the double nitrites are colourless or yellow, so that complex derivatives are evidently formed by it. In Balke and Smith's paper already mentioned (p. 51), various columbates, fluoro-columbates, and percolumbates are described, along with analogous tantalum compounds ; many have a complex composition. The columbium material used by them, as well as that similarly obtained from many different sources, was subjected to rigorous spectroscopic examination,<sup>60</sup> and it is shown that pure columbium solutions, quite free from titanium, give a yellow coloration on application of the hydrogen peroxide test, so that the presence of columbium vitiates this as a reaction for titanium.

#### Group VI.

The elucidation of the reactions involved in the contact process for the manufacture of sulphuric acid, when metallic oxides are used as catalysts, has given rise to a considerable amount of investigation, and, in particular, the equilibrium conditions in the dissociation of the sulphates of iron and of a good many other metals has been very fully studied.<sup>61</sup> Some of the results obtained indicate that the catalytic action of ferric oxide is not due to alternate reduction and oxidation, since sulphur dioxide by itself is without effect at the temperatures involved ; nor is the action due to the union of ferric oxide, sulphur dioxide, and oxygen, forming a ferric sulphate, since the concentration of sulphur trioxide at a given temperature is higher than what is produced by dissociation of ferric sulphate. The action would therefore appear to consist in the direct union of sulphur dioxide and oxygen, induced by some sort of condensation effect at the surface of the catalyst.

The dehydration of the ordinary crystallised thiosulphates is a matter of some difficulty, which formerly gave rise to divergent views

<sup>59</sup> *Ann. Report*, 1907, 59 ; G. Gain, *Compt. rend.*, 1907, 146, 403 ; *Ann. Chim. Phys.*, 1908, [viii], 14, 224 ; *A.*, ii, 284, 599.

<sup>60</sup> W. M. Barr, *J. Amer. Chem. Soc.*, 1908, 30, 1668 ; J. H. Hildebrand, *ibid.*, 1908, 30, 1662 ; *A.*, ii, 1045.

<sup>61</sup> G. Keppeler and others, *Zeitsch. physikal. Chem.*, 1908, 62, 89 ; *Zeitsch. angew. Chem.*, 1908, 21, 532, 537 ; L. Wohler and others, *Ber.*, 1908, 41, 703 ; *Zeitsch. physikal. Chem.*, 1908, 62, 641 ; *A.*, ii, 289, 290, 482, 581.

regarding the constitution of these salts; apparently, however, the direct preparation of the anhydrous salts is comparatively simple. By passing hydrogen sulphide over powdered sodium sulphide at  $300^{\circ}$ , dry sodium hydrosulphide is obtained, and from this the thiosulphate can be obtained by the action of air or oxygen at  $100\text{--}150^{\circ}$ .<sup>62</sup>

Most of the important work on chromium deals with the complex salts and similar substances derived from it. The complications and isomerism apparently extend to the hydroxides; the pure substance of "Guignet's green" is a hydroxide,  $\text{Cr}_4\text{O}_3(\text{OH})_6$ , which has the same composition as the greyish-violet hydroxide, but, whilst the former exhibits distinct vapour pressures of  $13\text{--}26$  mm. at temperatures between  $75^{\circ}$  and  $84^{\circ}$ , the latter has practically none.<sup>63</sup>

### *Group VII.*

There is little of moment to be noted here in connexion with the halogens; several papers have been published which deal with the details of electrolytic processes of preparation on the large scale, and call for no comment. One technical matter of general interest may, however, be referred to, namely, the preparation of dry calcium hypochlorite.<sup>64</sup> According to one process, this can be effected by acting on milk of lime with chlorine, evaporating the clear solution at a low temperature under diminished pressure so as to crystallise out the hypochlorite as quickly as possible, and dehydrating the crystallised salt, also under diminished pressure. An improvement consists in adding fresh quantities of lime and chlorine alternately, after the first chlorination, by which means it is possible to obtain a good yield of hypochlorite without evaporation. It is claimed that the dried salt is not deliquescent, and keeps well. It is, of course, much more efficient than bleaching powder, and, on treatment with hydrochloric acid, it gives nearly its own weight of chlorine. A substance of this kind should prove of considerable use in laboratory work.

The propriety of placing manganese in the seventh group of elements has been questioned,<sup>65</sup> on account of its almost complete lack of relationship with the halogens, and its great similarity to members of the eighth group. The difficulty is analogous to that which results when copper, silver, and gold are classed along with the alkali metals, and shows that Mendeléeff's original arrangement is not altogether a happy one; although the arrangement may occasionally serve for a rough classification (as in the present case), its use nowadays is hardly

<sup>62</sup> D.R.-P. 194881, 194882; *A.*, ii, 689.

<sup>63</sup> L. Wohler and W. Becker, *Zeitsch. angew. Chem.*, 1908, 21, 1600; *A.*, ii, 765.

<sup>64</sup> D.R.-P. 188524, 195896; *A.*, ii, 280, 692.

<sup>65</sup> H. Reynolds, *Chem. News*, 1907, 96, 260; *A.*, ii, 41.

justifiable. Many difficulties, such as those mentioned above, can be avoided by the use of longer periods.<sup>66</sup>

### Group VIII.

Interest in the metals of this group centres largely in the complex salts formed by the various members, and in the alloys and similar substances of which they form constituents; in both these departments there has been considerable activity during the year.

The rusting of iron seems to provide a never-ending problem, and different investigators continue to draw different conclusions as the result of their researches; several additional papers have recently appeared.<sup>67</sup> Two different problems are really involved in the discussion: one the behaviour of pure iron in presence of pure water and oxygen, and the other the behaviour of the different kinds of iron and its alloys in ordinary use. Owing to the great difficulty of getting reasonably homogeneous samples of pure iron (slight differences of composition may produce pronounced differences in the electrical conditions, etc.), the first problem is one regarding which it is very difficult to obtain a satisfactory decision, and it is one of relatively slight practical importance. The other, however, is a matter of the very greatest practical importance, and necessitates a study of the effects which variations in composition and in the attendant circumstances produce on the rate of rusting under ordinary conditions; the second of the papers to which reference has been made is an extensive investigation of this kind.

There is further evidence that platinum, when used as an anode in certain electrolytic processes, or otherwise submitted to the action of powerful oxidising agents, is not quite so resistant as is generally assumed,<sup>68</sup> so that the possibility of traces of platinum passing into solution in this way should not be overlooked. In consequence of the highly refractory qualities of iridium and rhodium, these metals seem to be almost ideal materials (except as regards price) for the production of crucibles and other apparatus.<sup>69</sup> "Boiling aqua regia, fused microcosmic salt, or other phosphates with frequent additions of carbon, strongly heated silica or silicates with a reducing agent, boiling lead at a white heat, boiling zinc, and molten nickel, iron, or

<sup>66</sup> See, for example, J. Walker, *Introduction to Physical Chemistry*; A. Werner, *Neuere Anschauungen auf dem Gebiete der anorganischen Chemie*.

<sup>67</sup> J. N. Friend, *J. Iron and Steel Inst.*, 1908, **77**, 1, 5; E. Heyn and O. Bauer, *Mitt. k. Mat.-prof.-Amt., Gross-Lichterfelde*, 1907, **26**, 1; *A.*, ii, 698, 849; W. A. Tilden, *Trans.*, 1908, **93**, 1356.

<sup>68</sup> *Ann. Report*, 1907, 73; C. Marie, *Compt. rend.*, 1908, **146**, 475; R. Ruer, *Deutsch. Elektrochem.*, 1908, **14**, 309, 633; *A.*, ii, 299, 601, 954.

<sup>69</sup> Sir W. Crookes, *Proc. Roy. Soc.*, 1908, **80**, A, 535; *A.*, ii, 702.

gold, are without effect on the crucible, which, after cleaning, retains its weight unchanged"; it is also passive under many other forms of chemical torture.

A very full investigation of the preparation and properties of the oxides of iridium has been carried out.<sup>70</sup> No monoxide,  $\text{IrO}$ , could be obtained, although such has been said to exist; the sesquioxide,  $\text{Ir}_2\text{O}_3$ , and the trioxide,  $\text{IrO}_3$ , could not be prepared in a pure condition; the dioxide,  $\text{IrO}_2$ , however, was obtained practically pure as a solid, and also in colloidal solution. When heated, the sesquioxide decomposes into dioxide and metal, some oxygen also being evolved.

HUGH MARSHALL.

<sup>70</sup> L. Wohler and W. Witzmann, *Zeitsch. anorg. Chem.*, 1908, **57**, 323; *A.*, ii 300.

## ORGANIC CHEMISTRY.

THE present report embraces the subject matter of four separate reports in previous annual volumes, dealing respectively with aliphatic, homocyclic, and heterocyclic compounds, and with stereochemistry. A glance at the Abstracts for the year 1908 will show that the space allotted to summaries of organic research is equal to that devoted to the résumés of all other sections of chemical activity. It is therefore inevitable that references to many valuable researches have been omitted, for only by making a selection of the year's output in organic chemistry has it been found possible to keep this report within reasonable bounds.

The theoretical views implied in the conventional structural formulæ have held their own with remarkable success throughout the development of organic chemistry, but their insufficiency to express the whole of the facts is becoming more obvious every year, and great uncertainty still prevails as to the nature of the changes to be made in order to bring certain of these formulæ into closer accordance with the experimental evidence. There can be little doubt that ideas derived from the consideration of plane formulæ require to be constantly verified by reference to the steric relationships of the component parts of the molecule of organic compounds. In certain cases the uncertainty or ambiguity attaching to the use of static conjugations has led to the adoption of dynamic formulæ. The direct application of such a physical hypothesis as that of the electron to organic chemistry would seem to be premature, probably because the hypothesis is still imperfectly developed, even in its simpler applications to the question of chemical affinity, but it has already furnished several suggestive qualitative ideas.

The recent developments in the theory of chemical valency implied in such conceptions as those of principal and subsidiary valencies and co-ordinated compounds have been adopted only in very few instances. Many of this year's researches have an important bearing on the valency of oxygen, and afford ample confirmatory evidence as to the quadri-valent nature of this element, particularly as manifested in the cyclic oxonium salts. On the other hand, no definite conclusion has been



reached in regard to the assumed tervalency of carbon in triphenylmethyl.

A striking feature of the year's work is the number of investigations dealing directly or indirectly with the influence of unsaturation, especially of the nature and arrangement of double linkings. The ideas put forward by Thiele, in 1899, recur frequently in recent work, notably those of partial valency and of the conjugation of double linkings. The first will be discussed below in connexion with the question of colour and fluorescence; the second finds an important place in many discussions as to the origin of colour and the reactivity of tautomeric compounds.

### *The Mechanism of Reactions.*

The great advances made in recent years in our knowledge of the structure of organic compounds have directed attention all the more vividly to the gaps which remain. This is especially the case with regard to reactions. The chemical equation only represents, as a rule, the initial and final stages, the mechanism by which the result is obtained remaining obscure, and only to be filled by the assumption of hypothetical intermediate products, the nature of which it is often very difficult to define. Much recent work has been directed to the elucidation of the mechanism of familiar reactions, such as the catalytic hydrogenation and dehydrogenation of organic compounds by metals, the reactions depending on the employment of magnesium organic compounds, the condensations in presence of aluminium chloride and of sodium ethoxide, and the formation of esters, etc.

### *Catalytic Action of Metals and Inorganic Substances.*

The remarkable results achieved by Sabatier and Senderens on the hydrogenation of organic compounds in the presence of finely-divided nickel at moderately high temperatures have led to numerous researches on the influence of catalysts in the synthesis and decomposition of organic substances.

Many aromatic compounds have been converted by the Sabatier and Senderens' method into the corresponding hydroaromatic derivatives. With hydrogen at 200° in the presence of nickel, *p*-benzoquinone and its homologues are reduced quantitatively to quinols. At 220—250° the quinols are decomposed into the corresponding phenols, and water is liberated, but at lower temperatures the quinols undergo further hydrogenation, becoming converted into *cyclohexane*-1:4-diols. Quinol itself at 160—170° gives a mixture of phenol, *cyclohexanol*,

and *cis*- and *trans*-cyclohexane-1:4-diols; at 130° this *cis*-modification is formed exclusively.

Catechol under similar conditions gives *cis*-cyclohexane-1:2-diol exclusively, resorcinol does not yield definite products, but pyrogallol is reduced to cyclohexane-1:2:3-triol.<sup>1</sup>

Other unsaturated rings may be hydrogenated by this method.

Furan at 170° gives rise to tetrahydrofuran,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{O}$ , together with a small amount of butyl alcohol and some saturated hydrocarbons.<sup>2</sup>

In some cases the reactions have showed signs of reversibility. The reverse change has been observed at 200—300° with indene and acenaphthene when reduced to hydrindene and tetrahydroacenaphthene, but decomposition products also arise. The hydrogenation of naphthalene to tetrahydronaphthalene which occurs at 200° is reversed at 300°.

In certain instances, hydrogenation,<sup>3</sup> under ordinary pressures in the presence of nickel, leads to the formation of secondary products, and even to the total suppression of the primary reaction. Quinoline, for example, is transformed into methylketol. When nickel oxide is employed as the catalyst at high temperatures (200—300°) and under high pressures (100—200 atmospheres), the hydrogenation runs its normal course, and the method has proved remarkably successful in yielding highly hydrogenated products, which are obtained only with considerable difficulty by other processes. Aniline yields principally hexahydroaniline, together with cyclohexylaniline and dicyclohexylamine. The last of these is the chief product of the hydrogenation of diphenylamine.

Quinoline is readily reduced, first to tetrahydroquinoline, and then to decahydroquinoline, an almost quantitative yield of the latter being obtained. Anthracene can be reduced in three successive stages to dihydroanthracene, tetrahydroanthracene, and, finally, perhydroanthracene.

Phenanthrene, which requires a higher temperature (320—370°/150—170 atmos.), is similarly reduced in stages to its dihydro-, tetrahydro-, and octahydro-derivatives, and, finally, perhydrophenanthrene; the yield of the last is so good that the method is recommended for the preparation of the compound.

When potassium phthalate is mixed with nickel oxide and heated in

<sup>1</sup> P. Sabatier and A. Muilhe, *Compt. rend.*, 1908, **146**, 437, 1193; *A.*, i, 278, 529.

<sup>2</sup> A. Bourguignon, *Bull. Soc. chim. Belg.*, 1908, **22**, 87; *A.*, i, 280.

<sup>3</sup> M. Padoa and U. Fabris, *Atti R. Accad. Lincei*, 1908, [v], **17**, i, 111; *A.*, i, 255.

hydrogen at 300°/100 atmos., an excellent yield of potassium *trans*-hexahydrophthalate (*trans*-cyclohexane-1 : 2-dicarboxylate) is produced. Sodium benzoate is readily converted into sodium hexahydrobenzoate (cyclohexanecarboxylate), the potassium salt being less affected.

Experiments conducted under ordinary pressures show that the nickel oxide acts as a catalyst only under high pressures. On the other hand, the presence of the catalyst is essential in the foregoing reductions, for heating with hydrogen alone under high pressure does not lead to the hydrogenation of the organic compounds.<sup>4</sup>

The use of metals as catalysts at high temperatures has led to the repetition and extension of certain old experiments on the use of platinum-black in reductions carried out on substances in solution. Compounds containing the ethylene linking are readily reduced with hydrogen in the presence of this catalyst even at the ordinary temperature. Ethyl oleate in ethereal solution gave ethyl stearate in quantitative yield, and oleyl and erucyl alcohols were similarly reduced to the fully saturated alcohols. Geraniol was converted into a mixture of  $\beta\zeta$ -dimethyloctane and  $\gamma\eta$ -dimethyloctanol. Cholesterol in ethereal solution furnished a dihydrocholesterol identical with  $\beta$ -cholestanol. Aromatic substances can be hydrogenated to hydroaromatic derivatives by this method, but somewhat less readily than by the high temperature processes; benzoic acid, for example, gives about 12 per cent. of cyclohexanecarboxylic acid.<sup>5</sup>

A powerful catalytic reducing agent has been prepared by adding hydrazine to a solution of palladium chloride and sodium protoalbinat, when the hydrosol of palladium is formed. The colloidal solution takes up a large amount of hydrogen, and when unsaturated substances are dissolved therein, and the liquid left in contact with hydrogen, the gas is quickly absorbed, and an energetic reduction is effected. Fumaric (maleic) and cinnamic acid in the form of their alkali salts are converted into succinic and  $\beta$ -phenylpropionic acids respectively. The method is applicable to the unsaturated glycerides occurring in many fats and oils; these substances are quantitatively converted into the saturated glycerides, this being the only process yet discovered which will effect this reduction at the ordinary temperature.<sup>6</sup>

Hydrogenation is not the only chemical change promoted by the catalytic influence of inorganic materials. Dehydration of alcohols

<sup>4</sup> W. N. Ipatieff, *Ber.*, 1908, **41**, 991; W. N. Ipatieff, W. Jakowleff, and L. Rakitin, *ibid.*, 1908, **41**, 996; W. N. Ipatieff and O. Philipoff, *ibid.*, 1908, **41**, 1001; *A.*, i, 330, 332, and 342.

<sup>5</sup> R. Willstätter and E. W. Mayer, *ibid.*, 1908, **41**, 1475, 2199; *A.*, i, 383, 636.

<sup>6</sup> C. Paal and J. Gerum, *ibid.*, 1908, **41**, 805, 2273; *A.*, ii, 392, i, 599; C. Paal and K. Roth, *ibid.*, 2283; *A.*, i, 599.

and similar substances is induced by certain oxides. Precipitated alumina and silica, when dried and gently calcined, promote the decomposition of ethyl alcohol into ethylene and water at temperatures much below those at which heat alone would be effective in decomposing this substance. At  $280^{\circ}$  the alcohol is quantitatively decomposed into water and ethylene. Prolonged calcination diminishes very considerably this catalytic power, for after being heated at a white heat, the oxides have no effect on the alcohol below  $400^{\circ}$ , and then only a small amount of ethylene is produced.

At  $300^{\circ}$  in the presence of gently-calcined alumina, ether is decomposed into ethylene and water, the reaction being recommended as a process for preparing this hydrocarbon. Acetic and propionic acids at  $350^{\circ}$  give respectively acetone and methyl ethyl ketone, together with carbon dioxide and water. Alumina also induces the elimination of hydrogen halides: at  $280^{\circ}$  chloropropane gives propylene, and ethylene dichloride yields vinyl chloride.

Carefully-calcined gypsum promotes the decomposition of alcohol at  $420^{\circ}$ , 90 per cent. of the gas evolved being ethylene and the rest hydrogen. Anhydrite has no effect below  $460^{\circ}$ . Aluminium silicate and kaolin have been shown to possess in some degree this catalytic power, which is somewhat diminished by calcination.<sup>7</sup>

A few general principles are apparent. When heated alone the primary aliphatic alcohols decompose at a red heat into (i) water and an olefine and (ii) hydrogen and an aldehyde, but they show no appreciable decomposition below  $400^{\circ}$ . In contact with finely-divided copper, nickel, cobalt, iron, and platinum, the alcohols undergo dehydrogenation at about  $350^{\circ}$ , the products being hydrogen and an aldehyde. At the same temperature, certain oxides, and particularly alumina, induce dehydration, the products now being water and an olefine.

#### *The Grignard Reaction.*

Although every year sees a great increase in the applications of the Grignard reaction in the synthesis of organic compounds, the exact mechanism of the process is even yet imperfectly understood, especially in respect of the true nature of the intermediate additive products. The complexes which the reagent forms with ether are generally uncrystallisable, but it has now been found <sup>8</sup> that by the employment of amyl ether in place of ethyl ether, crystalline compounds, such as  $(C_5H_{11})_2O \cdot CH_3MgI$ , may be prepared. Whilst magnesium alkyl halides can also add on a second molecule of ether, the additive compounds with tertiary amines never contain more than one mol. of the

<sup>7</sup> J. B. Senderens, *Compt. rend.*, 1908, **146**, 125, 1211; *Bull. Soc. chim.*, 1908, [iv], **3**, 633; *A.*, i, 494, 495, i, 168.

<sup>8</sup> T. Zerewitinoff, *Ber.*, 1908, **41**, 2244; *A.*, i, 616.

latter. They are, however, capable of combining also with a molecule of ether, yielding mixed ether-amine complexes. Replacement of ether by amine, or conversely, may take place, the change proceeding in the one or the other direction according to the relative stability of the resulting additive compounds, as shown by thermochemical measurements. Ethers are not capable of expelling aliphatic amines, the final product being one containing one mol. of ether and one mol. of amine.<sup>9</sup> It is concluded from these results that addition takes place at two dissimilar positions in the molecule of the magnesium organic halide.

The Grignard reaction may also take place, although less readily and less smoothly, in the absence of ether or even of a solvent. Aromatic halogen compounds combine with magnesium almost quantitatively on heating, and the products react with water, yielding the parent hydrocarbon. Aryl chlorides, and the halides of alkyls lower in the series than amyl, must be heated in a sealed tube at 270°. Bromo- and iodo-benzene yield some diphenyl as well as benzene, and the lower alkyl iodides give rise to hydrogen and unsaturated hydrocarbons in addition to the principal product. These results indicate that the first stage in the reaction is the direct addition of magnesium to the alkyl or aryl halide, and that the formation of an oxonium compound in the presence of ether is a subsequent stage.<sup>10</sup>

Other metals behave in a similar manner to magnesium when heated with organic halides. The products obtained with aluminium, indium, and thallium yield the hydrocarbons on treatment with water.<sup>11</sup>

The varying degree in which metals of different groups are capable of replacing magnesium in the Grignard synthesis has been studied and tabulated.<sup>12</sup>

From the action of sodium and alkyl halides on certain compounds, the intermediate formation of sodium alkyl seems to be established. Thus acetophenone, *iso*amyl iodide, and sodium yield phenylmethyl*iso*-amylcarbinol,  $\text{OH} \cdot \text{CPhMe} \cdot \text{C}_5\text{H}_{11}$ . A mixture of sodium with a mercury dialkyl, which must contain a mercury alkyl compound, may also be used. Thus mercury diethyl, sodium, and benzaldehyde react in ether to form phenylethylcarbinol, identical with that obtained by means of Grignard's reagent. Carbon dioxide forms the corresponding carboxylic acid with a mixture of sodium and mercury alkyl. Aromatic acids may be prepared by the action of carbon dioxide on the same mercury alkyl-sodium mixture in presence of an aromatic

<sup>9</sup> W. Tschelinzeff, *Ber.*, 1908, **41**, 646; *A.*, i, 254.

<sup>10</sup> J. F. Spencer and E. M. Stokes, *Trans.*, 1908, **93**, 68; J. F. Spencer and M. S. Crewdson, *ibid.*, 1821.

<sup>11</sup> J. F. Spencer and M. L. Wallace, *ibid.*, 1908, **93**, 1827.

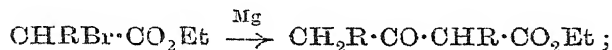
<sup>12</sup> J. Zeltner, *J. pr. Chem.*, 1908, [ii], **77**, 393; *A.*, i, 401.

hydrocarbon. When a side-chain is pre-ent, the carboxyl group enters this, so that, for instance, *m*-xylene gives *m*-tolylacetic acid, and ethylbenzene gives  $\alpha$ -phenylpropionic acid.<sup>13</sup>

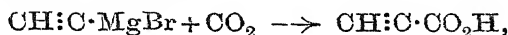
Magnesium aryl chlorides, which cannot be prepared by the ordinary method, are readily obtained when the reaction between the metal and the aryl chloride is induced by the introduction of a more reactive halide, such as ethyl iodide.<sup>14</sup>

The chlorine in chlorodimethyl ether is not replaceable by magnesium, even when iodine is added, but this ether reacts vigorously with magnesium phenyl bromide, giving benzyl methyl ether, and this reaction is found to be general.<sup>15</sup>

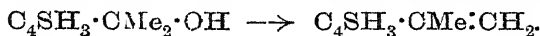
Among new Grignard syntheses to be noted are the production of  $\beta$ -ketonic esters from  $\alpha$ -halogen fatty esters<sup>16</sup>:



the production of propiolic acid by the action of carbon dioxide on magnesium acetylene bromide<sup>17</sup>:

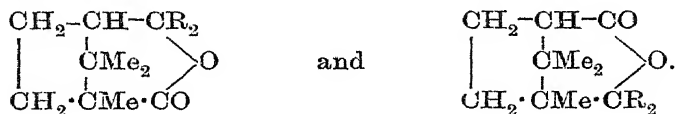


and the preparation of thienyl derivatives from iodothiophen.<sup>18</sup> Thus 2-iodothiophen and acetone condense with magnesium in ethereal solution, yielding thienyldimethylcarbinol and  $\beta$ -thienylpropylene:



Anhydrides of dibasic acids generally react with Grignard's reagent in such a way that both the carbonyloxygen atoms are replaced by alkyl or amyl groups, succinic anhydride, for instance, giving compounds of

the type  $\begin{array}{c} \text{CH}_2 \cdot \text{CR}_2 \cdot \text{OH} \\ | \\ \text{CH}_2 \cdot \text{CR}_2 \cdot \text{OH} \end{array}$  Camphoric anhydride, on the other hand, reacts abnormally, only one oxygen atom being replaced, giving a mixture of the isomeric dialkyl-campholides<sup>19</sup>:



<sup>13</sup> P. Schorigin, *Ber.*, 1908, **41**, 2711, 2717, 2723; *A.*, i, 866, 881, 886.

<sup>14</sup> A. Hesse, D.R.-P. 189476, *A.*, i, 592.

<sup>15</sup> A. Reyehler, *Bull. Soc. chim.*, 1907, [iv], 1, 1198; *A.*, i, 159; J. L. Hamonet, *ibid.*, 1908, [iv], 3, 254; *A.*, i, 242.

<sup>16</sup> J. Zeltner, *Ber.*, 1908, **41**, 589; *J. pr. Chem.*, 1908, [ii], 78, 97; *A.*, i, 243, 759.

<sup>17</sup> B. Oddo, *Gazzetta*, 1908, **38**, i, 625; *A.*, i, 748.

<sup>18</sup> V. Thomas, *Compt. rend.*, 1908, **146**, 642; *A.*, i, 360.

<sup>19</sup> J. Houben and A. Hahn, *Ber.*, 1908, **41**, 1580; *A.*, i, 539.

*o*-Phthalaldehyde forms dihydroxyalkylbenzenes, which on distillation pass into 1:3-dialkylphthalans<sup>20</sup>:



Since *C*-alkylated primary bases may be prepared by the action of magnesium organic compounds on Schiff's bases, the hydramides,  $\text{CHR:N}\cdot\text{CHR:N}\cdot\text{CHR}$ , which contain the characteristic grouping of Schiff's bases twice, have been examined from the same point of view. The reaction is, however, abnormal, addition at the unsaturated groupings being accompanied by the resolution of a carbon-nitrogen single linking, according to two different schemes:

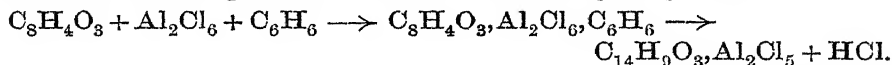
(I).  $\text{CHPh(N:CHPh)}_2$  with  $\text{MgMeI}$ , followed by water,  $\longrightarrow$   $\text{CHMePh}\cdot\text{NH}_2 + \text{NH(CHMePh)}_2$ .

(II).  $\text{CHPh(N:CHPh)}_2 \longrightarrow \text{CHO}\cdot\text{Ph} + \text{NH}_2\cdot\text{CHMePh}$ ,  
magnesium aryl halides reacting only according to the second scheme.<sup>21</sup>

A reducing action of magnesium organic compounds has also been observed in the aliphatic series. Thus ethyl hydroxypivalate,  $\text{OH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CO}_2\text{Et}$ , reacts with magnesium ethyl bromide, the ketone formed being partly reduced, especially at low temperatures, with evolution of ethylene, forming  $\beta\beta$ -dimethylpentane- $\alpha\gamma$ -diol,  $\text{CH}_2\text{Me}\cdot\text{CH(OH)}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$ .

### *The Friedel and Crafts Reaction.*

In the condensation of phthalic anhydride with benzene, it is found that the presence of exactly one (double) molecule of aluminium chloride is necessary to bring about the reaction, and the formation of an intermediate product is thus rendered highly probable:



Naphthalene will not readily condense with phthalic anhydride in an indifferent solvent under the influence of aluminium chloride, but when benzene or one of its homologues is added, the whole of the naphthalene reacts to form naphthoylbenzoic acid, even although the benzene may be in great excess. Naphthalene (or anthracene) is thus capable of displacing benzene from the additive product.<sup>22</sup>

When nitro-compounds are condensed with hydrocarbons, the nitro-group is eliminated, and some oxidation takes place. Thus trichloro-nitromethane and benzene react in presence of aluminium chloride, giving triphenylmethane and some triphenylcarbinol, the latter

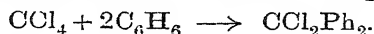
<sup>20</sup> F. Nelken and H. Simonis, *Ber.*, 1908, **41**, 986; *A.*, i, 348.

<sup>21</sup> M. Busch and L. Leefhelm, *J. pr. Chem.*, 1908, [ii], **77**, 1, 20; *A.*, i, 151, 158.

<sup>22</sup> G. Heller and K. Schülke, *Ber.*, 1908, **41**, 3627; *A.*, i, 994.

produced by oxidation. Ethyl nitrate under similar conditions acts as a nitrating agent, giving nitrobenzene with benzene. Benzene, amyl nitrite, and aluminium chloride give small quantities of nitrosobenzene.<sup>23</sup>

When benzene is condensed with carbon tetrachloride, the chlorine atoms are replaced in pairs, the first product capable of isolation being dichlorodiphenylmethane, no trichloro-compound being detected :



A study of the behaviour of halogen derivatives of benzene in this reaction, the condensation product being subsequently boiled with sulphuric and acetic acids, leads to the conclusion that the substitution is not simultaneous, but that the velocity of replacement of the second chlorine atom is very great.<sup>24</sup>

### *The Claisen Condensation.*

Although several different explanations of the Claisen condensation have been suggested by different workers, that put forward by Claisen in 1887 is still the most generally accepted, namely, that the ester first forms an additive compound with sodium ethoxide. A study of the velocity of formation of ethyl acetonyloxalate from acetone, ethyl oxalate, and sodium ethoxide in alcoholic solution, as measured by the colour produced by ferric chloride after neutralisation, is interpreted by Clark as favouring this explanation when the dependence of the velocity on the concentration of the reacting substances is taken into account.<sup>25</sup> A quantitative comparison of different reacting esters, and of the influence of catalysts shows that, as required by this hypothesis, the addition of alcoholic sodium ethoxide greatly accelerates the reaction between ketones and esters in presence of sodium.<sup>26</sup>

On the other hand, experiments with menthone and pulegone, reacting with amyl nitrite (instead of a carboxylic ester) in presence of sodium ethoxide, shows that the group  $\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}\cdot$  is attacked, not at the  $\cdot\text{CH}_2\cdot\text{CO}\cdot$  point, as might be expected, but at the  $\cdot\text{CO}\cdot\text{CH}\cdot$  group.<sup>27</sup> A discussion of the mechanism of this reaction leads to the conclusion that, as suggested by several authors, the metallic derivative of the ketone must react to some extent in the *C*-form. In other words, there must be in the solution a real or virtual equilibrium (that is, either an equilibrium of the ions or one within the molecule itself,

<sup>23</sup> E. Bodtker, *Bull. Soc. chim.*, 1908, [iv], 3, 726 ; *A.*, i, 621.

<sup>24</sup> J. Boeseken, *Rec. trav. chim.*, 1908, 27, 5 ; *A.*, i, 189.

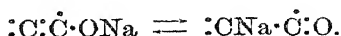
<sup>25</sup> R. H. Clark, *J. Physical Chem.*, 1908, 12, 1 ; *A.*, i, 124.

<sup>26</sup> J. B. Tingle and E. E. Gorsline, *Amer. Chem. J.*, 1908, 40, 46 ; *A.*, i, 732.

<sup>27</sup> R. W. L. Clarke, A. Lapworth, and E. Wechsler, *Trans.*, 1908, 93, 30.



without actual dissociation) between the *C*-sodium and the *O*-sodium derivatives :



These *C*-metallic derivatives must react in a similar manner to organo-metallic compounds, and the aceto-acetic ester synthesis thus becomes a particular case of the reaction between esters and organo-metallic compounds. The authors give a theoretical discussion of the whole question on this basis.

The reversibility of the acetoacetic condensation, that is, the decomposition of the diketone by sodium ethoxide, is found to depend on the acidity of the compound, the more acid its character the greater being its stability. Thus methyl  $\gamma$ -acetyldimethylacetoacetate,  $CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot CMe_2 \cdot CO_2Me$ , is hardly attacked by sodium ethoxide even on boiling, but when the acidity of the central methylene group is reduced by methylation, as in ethyl trimethylacetonedicarboxylate,  $CO_2Et \cdot CHMe \cdot CO \cdot CMe_2 \cdot CO_2Et$ , this power of resistance disappears.<sup>28</sup>

#### *Esterification and Catalysis.*

Perhaps the most interesting problems in connexion with the formation of esters from acids and alcohols are the influence of catalysts on the velocity of the reaction and the effect of steric hindrance, both of which have received attention during the past year. The influence of catalysts in the formation of ethyl benzoate has been the subject of a very extensive series of measurements,<sup>29</sup> the results of which prove that a large number of factors enter into the process, but do not allow any general conclusion to be drawn. The efficiency of the catalyst could not be shown to depend on its degree of ionisation. The effect of neutral salts is also a complex one, and dehydration plays a considerable part, as urged by H. E. Armstrong in numerous papers.

An important theoretical paper has quite recently appeared dealing with the general catalytic function of hydrogen ions.<sup>30</sup> The treatment of the subject is mainly physical and mathematical; so far as esterification and ester hydrolysis are concerned, the most striking suggestion is that the addition of water to an acid in a less basic solvent diminishes the availability of the acid, or diminishes the

<sup>28</sup> W. Dieckmann and A. Kron, *Ber.*, 1908, **41**, 1260; *A.*, i, 388.

<sup>29</sup> I. K. Phelps, M. A. Phelps, E. A. Eddy, H. E. Palmer, R. W. Osborne, and R. Smillie, *Amer. J. Sci.*, 1908, [iv], **25**, 39; **26**, 281, 290, 296; *A.*, i, 166, 789, 790.

<sup>30</sup> A. Lapworth, *Trans.*, 1908, **93**, 2203; E. Fitzgerald and A. Lapworth, *ibid.*, 2163.

concentration of those "ions" which bring about catalysis. These ions are not identical with the "hydrogen ions" to which the electrical conductivity is due, which are probably complex. The ideas propounded are likely to form the basis of an interesting discussion of the nature of catalysis.

Many experiments on the catalytic function of acids in the hydrolysis of imino-esters,<sup>31</sup> the formation of oximes,<sup>32</sup> and the acetylation of amino-groups<sup>33</sup> have also been made, and the importance of considering the basic character of the substances undergoing change is in all cases pointed out.

An examination of the absorption spectra of certain unsaturated ketonic compounds, of which cinnamylideneacetic acid and cinnamylideneacetone are types, leads to conclusions of some interest in connexion with the different rate of esterification of different acids.<sup>34</sup> It has been conjectured that the process of esterification depends on the residual affinity of the carbonyl group in the acid, to which the alcohol adds itself. The spectroscopic evidence shows that the residual affinity of a carbonyl group is greatest when the atom attached to the hydroxylic oxygen is not ionised, the effect of adding an acid, and thus diminishing the ionisation of the organic acid, therefore being to increase the residual affinity of the carbonyl. In connexion with this, the effect of small quantities of hydrogen chloride on the spectra of aromatic amino-aldehydes and -ketones has been examined. The development of a new band indicates that the residual affinity of the amino-group is increased by such addition, and this would account for the catalytic action of acids in the acetylation of such compounds.<sup>35</sup>

The effect of steric hindrance is illustrated by experiments with arylated acetic acids.<sup>36</sup> Triphenylacetic acid is much more difficult to esterify than trialkylated acetic acids, the introduction of the third phenyl group having also a much greater effect than that of the first or second. The same thing is shown by a comparison of benzoic acid,  $\text{C}_6\text{H}_5\cdot\text{C}(\text{OH})\cdot\text{CO}_2\text{H}$ , with glycollic and mandelic acids, the phenyl group having a far greater influence than hydroxyl in retarding esterification.

<sup>31</sup> J. Stieglitz, *Amer. Chem. J.*, 1908, **39**, 29, 166; *A.*, i, 167, 168.

<sup>32</sup> S. F. Acree, *ibid.*, 300; *A.*, i, 169.

<sup>33</sup> A. E. Smith and K. J. P. Orton, *Trans.*, 1908, **93**, 1242.

<sup>34</sup> E. C. C. Baly and K. Schaefer, *ibid.*, 1808.

<sup>35</sup> E. C. C. Baly and E. G. Marsden, *ibid.*, 2108.

<sup>36</sup> J. Gyr, *Ber.*, 1908, **41**, 4308; *A.*, 1909, ii, 33.

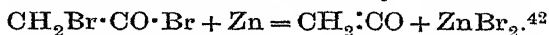
*Simple Hydrocarbons and Aliphatic Derivatives.*

The complicated and much discussed problem of the behaviour of the simpler saturated and unsaturated hydrocarbons at high temperatures has been submitted to further experiment, with the result that methane is found to be always the main product of the thermal decomposition of ethane, ethylene, and acetylene. Methane itself decomposes directly into carbon and hydrogen, mainly at the contact with the walls of the vessel, whereas the other hydrocarbons undergo decomposition throughout their mass. Acetylene is only produced in notable quantity from ethylene.<sup>37</sup> The authors suggest that such residues as  $\cdot\text{CH}_2$  and  $\cdot\text{CH}$  have at least a momentary existence, and give rise to methane by combination with hydrogen. All these processes take place slowly in comparison with those of combustion.

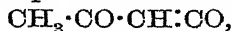
The direct formation of methane from carbon and hydrogen, which was questioned by Mayer and Altmayer,<sup>38</sup> has now been placed beyond doubt by the production of 73 per cent. of the theoretical quantity of methane by the action of hydrogen on purified carbon.<sup>39</sup>

Aliphatic derivatives of great complexity are of frequent occurrence in recent chemical literature, and the need of further classification has been felt. Meldola<sup>40</sup> has proposed the grouping of open-chain systems into those composed respectively of similar and dissimilar atoms, and has suggested for these, from analogy to homocyclic and heterocyclic compounds, the designations "homocatenic" and "heterocatenic," the latter including, for instance, the long chain-systems of the polypeptides.

The interesting and highly reactive group of the ketens has been further studied. The parent substance, keten,  $\text{CH}_2\cdot\text{CO}$ , the isolation of which was announced last year<sup>41</sup> as a product of the thermal decomposition of acetic anhydride, has been proved to have the constitution then assigned to it. It has also been found possible to prepare it by the general method for the production of ketens, namely, by the action of zinc on bromoacetyl bromide :



The simplest polymerisation product of keten is acetylketen,



a colourless liquid, which reacts with water to form acetoacetic acid,

<sup>37</sup> W. A. Bone and H. F. Coward, *Trans.*, 1908, **93**, 1197.

<sup>38</sup> *Ann. Report*, 1907, 74.

<sup>39</sup> W. A. Bone and H. F. Coward, *Trans.*, 1908, **93**, 1975.

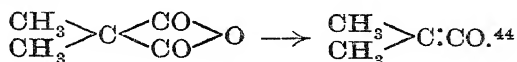
<sup>40</sup> *Trans.*, 1908, **93**, 1665, footnote.

<sup>41</sup> *Ann. Report*, 1907, 85.

<sup>42</sup> H. Staudinger and H. W. Klever, *Ber.*, 1908, **41**, 594 ; *A.*, i, 246.

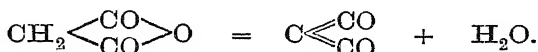
and with aniline to form acetoacetanilide. With phenylhydrazine it forms a phenylhydrazone-phenylhydrazide.<sup>43</sup>

A new method for the preparation of dimethyl- and diethyl-keten has been found in the decomposition of di-substituted malonic anhydrides by heat:



The anhydrides required for the above reaction are prepared by heating the semi-chlorides of the acids; they are highly polymerised. A second method of preparation is that of treating the acid dichlorides with aqueous pyridine.<sup>45</sup>

When, instead of dialkylmalonic acids, malonic acid is treated by a method for producing the anhydride, as by the action of acid chlorides on silver malonate, or of silver oxide on malonyl dichloride, keten is not produced, but in its place carbon suboxide is obtained, the hypothetical intermediate anhydride thus decomposing according to the equation:



Dibromomalonyl dichloride,  $\text{CBr}_2(\text{COCl})_2$ , readily reacts with zinc, giving a good yield of carbon suboxide.<sup>46</sup>

These methods of preparation indicate that carbon suboxide is itself to be regarded as a keten. It combines with formic and acetic acids to form compounds in which the characteristic structure appears to be preserved, the formic acid compound, for instance, reacting in accordance with the formula  $\begin{array}{c} \text{CO}_2\text{H} \\ \diagup \\ \text{O} \end{array} \text{C:C:C} \begin{array}{c} \text{CO}_2\text{H} \\ \diagdown \\ \text{O} \end{array}$ . The acetic acid compound breaks up in a remarkable manner on heating, yielding acetic anhydride and a syrup which is completely converted by water into malonic acid. Whilst this substance may be only a polymeride of carbon suboxide, it is at least possible that it may represent the hitherto unknown malonic anhydride,  $\text{CH}_2 \begin{array}{c} \text{CO} \\ \diagup \\ \text{O} \\ \diagdown \\ \text{CO} \end{array}$ .<sup>47</sup>

A comparison of the properties of the ketens now known has suggested their classification in two groups, of which the first includes keten and its monoalkyl derivatives and carbon suboxide, all of which are colourless, incapable of autoxidation, and are polymerised by pyridine. They are termed aldoketens. The members of the second group, consisting of the di-substituted ketens, are coloured, undergo

<sup>43</sup> F. Chick and N. T. M. Wilshire, *Trans.*, 1908, **93**, 946.

<sup>44</sup> H. Staudinger and E. Ott, *Ber.*, 1908, **41**, 2208, 3829; *A.*, i, 602, 939.

<sup>45</sup> A. Einhorn, *Annalen*, 1908, **359**, 145; *A.*, i, 312.

<sup>46</sup> H. Staudinger and S. Bereza, *Ber.*, 1908, **41**, 4461; *A.*, 1909, i, 83.

<sup>47</sup> O. Diels and L. Lalin, *ibid.*, 1908, **41**, 3426; *A.*, i, 939

autoxidation, yield keten bases with pyridine, and, unlike the aldoketens, yield additive products with benzylideneaniline and quinone containing the groups C:N and C:O respectively. They are termed keto-ketens. Thus diphenylketen combines with quinones to form  $\beta$ -lactones, such as  $\text{O:C}_6\text{H}_4\text{C}(\text{CPh}_2)\text{CO}$ , which decompose when heated, giving derivatives of diphenylquinonemethane. The additive compound with dibenzylideneacetone loses carbon dioxide spontaneously, the product being  $\alpha\epsilon$ -diphenyl- $\gamma$ -diphenylmethylene- $\Delta^{\alpha\delta}$ -pentadiene,

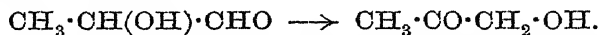


a compound belonging to a class which may be described as acyclic fulvenes, from their resemblance to the fulvenes :

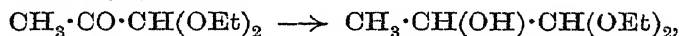


Their colour is much less intense than that of the fulvenes, as might be expected from the absence of the ring structure.<sup>48</sup>

Previous attempts to prepare the aldehyde of lactic acid, the simplest methyl sugar, have failed, and it has been conjectured that it must isomerise to acetol :

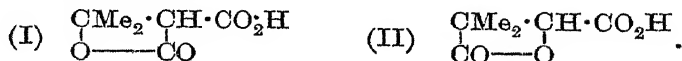


It has now been found that its acetal may be prepared by the reduction of methylglyoxalacetal :



and the latter compound, which may be regarded as the methyl ketone of diethoxyacetic acid, may be prepared by the action of magnesium methyl iodide on the amide of that acid. It was found better to employ the piperidide, from which the acetal was readily prepared. The lactaldehydeacetal obtained on reduction was readily decomposed by acids, yielding the bimolecular crystalline form of lactaldehyde, which slowly dissociates in solution, as shown by determinations of the molecular weight.<sup>49</sup>

The condensation of malonic acid with acetone in the presence of acetic anhydride leads to the formation of the  $\beta$ -lactone of  $\beta$ -hydroxy-isopropylmalonic acid (I). It is remarkable that the only other aliphatic  $\beta$ -lactone known is an isomeride of this (II) derived from  $\alpha\epsilon$ -dimethylmalic acid :<sup>50</sup>



<sup>48</sup> H. Staudinger, *Ber.*, 1908, **41**, 906, 1355, 1493; *A.*, i, 318, 410, 411.

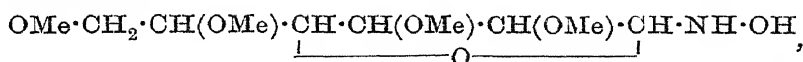
<sup>49</sup> A. Wohl, *ibid.*, 1908, **41**, 3599; *A.*, i, 941.

<sup>50</sup> A. N. Meldrum, *Trans.*, 1908, **93**, 598.

The oxidation of butyric acid to acetone is probably typical of a number of oxidations which take place in the living plant, and an examination of this reaction proves that it is readily effected in the case of the higher acids. Thus lauric acid is oxidised by hydrogen peroxide: an unstable ketonic acid is the first product, readily passing into methyl *n*-nonyl ketone.<sup>50a</sup>

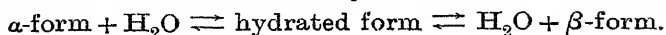
### Carbohydrates.

Further evidence for the  $\gamma$ -oxidic formula for glucose and other reducing sugars has now been brought forward. Thus glucoseanilide exists in two stereoisomeric modifications, and on methylation yields tetramethyl glucoseanilide, identical with that prepared from tetramethyl glucose. Similarly, glucoseoxime is methylated to tetramethyl glucoseoxime methyl ether. That the tetramethyl derivatives possess the  $\gamma$ -oxidic structure is shown by the impossibility of further methylation, since an aldehydic derivative would allow of the introduction of two more methyl groups. The oxime therefore has the constitution:

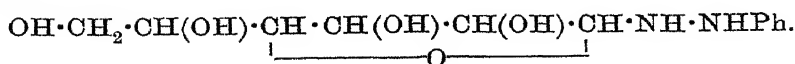


and exists in two stereoisomeric modifications. A similar result was obtained with the anilides. The results of acetylation and reduction of glucoseoxime are difficult to reconcile with the formula proposed, but it is pointed out that the reagents used in these cases are more liable to cause isomeric change than the methyl iodide and silver oxide used in methylation.<sup>51</sup>

The mutarotation of lactose has been shown to be due to the gradual establishment of equilibrium between the hydrated  $\alpha$ -modification and the anhydrous  $\beta$ -modification. In the scheme below, the first equilibrium is attained instantly, the second only slowly:<sup>52</sup>



The change of dextrophenylhydrazone into the isomeric modification is accelerated by acids and retarded by alkalis. It is suggested that, if not *syn*- and *anti*-modifications, one of the isomerides may be the true hydrazone and the other one of the stereoisomeric forms of the  $\gamma$ -oxidic derivative, as suggested by Irvine for the oxime and anilide:<sup>53</sup>



<sup>50a</sup> H. D. Dakin, *J. Biol. Chem.*, 1908, **4**, 221; *A.*, **i**, 134.

<sup>51</sup> J. C. Irvine and A. M. Moodie, *Trans.*, 1908, **93**, 95; J. C. Irvine and R. Gilmour, *ibid.*, 1429.

<sup>52</sup> C. S. Hudson, *J. Amer. Chem. Soc.*, 1908, **30**, 1767; *A.*, **i**, 952.

<sup>53</sup> R. Behrend and F. Lohr, *Annalen*, 1908, **362**, 78; *A.*, **i**, 765.

When pure glycerose is polymerised by contact with colloidal barium carbonate in methyl alcohol, a pentose is formed. It thus appears that polymerisation does not take place directly, but that the simple sugar is first depolymerised to formaldehyde.<sup>54</sup> The view has also been taken that alcoholic fermentation consists in a breaking down of the sugar molecule to formaldehyde, followed by the conversion of this into alcohol and carbon dioxide. Formaldehyde is converted by zinc carbonate into formic acid, methyl alcohol, acetol, and methyl-ketol. Zinc dust reacts in the same way, the product then including several sugars, among which  $\beta$ -acrose could be detected, and polyhydroxy-acids. Dextrose and zinc dust yield formic acid, diacetyl, methylglyoxal, and polyhydroxy-acids, but no methyl alcohol.<sup>55</sup>

The action of dilute alkalis on the hexoses has been further studied. Since alkalis have been found to convert aldoses partly into the corresponding hexoses, it should be found that *l*-gulose and *l*-idose should be converted into *l*-sorbose, and this was confirmed. As might be expected from the fact that dextrose and lævulose form an equilibrium mixture in alkaline solutions, these two sugars are found to behave similarly on prolonged treatment with dilute alkali. The principal product of decomposition is *i*-lactic acid, but polyhydroxy-acids and small quantities of formic acid, carbon dioxide, and alcohol are also formed.<sup>56</sup> The lactic acid formed in these experiments is almost certainly produced from methylglyoxal, dihydroxyacetone, or glyceraldehyde. An examination of the polyhydroxy-acids, however, leads to conclusions which are not in accordance with those of Nef,<sup>57</sup> saccharins with less than six carbon atoms being undoubtedly present. Nef's views, also, would indicate that *iso*-saccharinic acid should be readily obtained from lævulose, but this is not the case, only a very small yield being obtained. On the other hand, lactose gives a considerable yield of *isosaccharinic acid*.<sup>58</sup>

Of other carbohydrate problems, that which has led to the most discussion is the question of the chemical behaviour of cellulose, especially on esterification. Analyses of several anhydrous polysaccharides indicate that the generally-accepted formula for starch, cellulose, etc.  $(C_6H_{10}O_5)_n$ , is incorrect, and should be replaced by  $(C_6H_{10}O_5)_n \cdot H_2O$ . In raffinose, melezitose, and mannasaccharide,  $n = 3$ ; in inulin,  $n = 6$ .<sup>59</sup>

<sup>54</sup> C. Neuberg, *Biochem. Zeitsch.*, 1908, 12, 337; *A.*, i, 765.

<sup>55</sup> W. Lob, *ibid.*, 78, 466; *A.*, i, 715, 765.

<sup>56</sup> J. Meisenheimer, *Ber.*, 1908, 41, 1009; *A.*, i, 319.

<sup>57</sup> *Ann. Report*, 1907, 87; also *Annalen*, 1907, 357, 214; *A.*, i, 5.

<sup>58</sup> H. Kiliani, *Ber.*, 1908, 41, 469; *A.*, i, 246.

<sup>59</sup> H. Kiliani, *Chem. Zeit.*, 1908, 32, 366; *A.*, i, 320.

Cellulose formate is prepared by the action of formic and sulphuric acids on cellulose, but the number of formyl groups introduced is as yet undetermined.<sup>60</sup> A new acetylating agent, by means of which three acetyl groups are introduced, consists of 100 grams of glacial acetic acid, 50 grams of zinc chloride, and 100 grams of acetic anhydride. It does not react with starch.<sup>61</sup> When cellulose is heated with nitric acid and acetic anhydride, the latter being in excess, only nitrates are obtained, unless sulphuric acid is also present, when some of the nitrate groups are removed and acetoneitrates are produced.<sup>62</sup> When mixtures of anhydrous sulphuric and nitric acids, the latter in large excess, are used, the cellulose nitrate always contains less nitrate groups than when more dilute acid is employed.<sup>63</sup>

Agreement has not yet been reached between different observers as to the true nature of "soda-cellulose." Whilst one observer finds a distinct break in the curve representing the partition of sodium hydroxide between cellulose and water, at the composition corresponding with the formula  $C_{12}H_{10}O_{10}Na$ ,<sup>64</sup> another, making use of the former data as well as of new measurements, concludes that no definite composition can be assigned to the solid substance, but that the process is one of adsorption, closely resembling the behaviour of palladium towards hydrogen, and probably susceptible of the same physical explanation.<sup>65</sup>

#### *Isomeric Change and Tautomerism.*

The influence of catalytic agents in bringing about isomeric change, as shown by the mutarotation of nitrocamphor, has been investigated in various solvents.<sup>66</sup> That the presence of a catalyst is essential, and that an ionising solvent is not itself capable of bringing about the change, is shown by the complete arrest of mutarotation when carbonyl chloride is added. This reagent combines with the traces of ammonia or amines present in most of the solutions, and thus destroys their catalytic function. The addition of acids does not have the same effect, as neutral salts also exert an accelerating action.

A systematic review of the different forms of structural isomerism has been given by the original author of the theory of tautomerism.<sup>67</sup>

<sup>60</sup> J. P. Bemberg, D.R.-P. 189836, 189837; *A.*, i, 321.

<sup>61</sup> D. J. Law, *Chem. Zeit.*, 1908, **32**, 365; *A.*, i, 321.

<sup>62</sup> E. Berl and W. Smith, jun., *Ber.*, 1908, **41**, 1837; *A.*, i, 505.

<sup>63</sup> B. Rassow and W. v. Bongé, *Zeitsch. angew. Chem.*, 1908, **21**, 732; *A.*, i, 394.

<sup>64</sup> W. Vieweg, *Ber.*, 1908, **41**, 3269; *A.*, i, 857.

<sup>65</sup> O. Miller, *ibid.*, 4297; *A.*, 1909, i, 13.

<sup>66</sup> T. M. Lowry and E. H. Magson, *Trans.*, 1908, **93**, 107, 119.

<sup>67</sup> C. Laar, *J. pr. Chem.*, 1908, [ii], **78**, 165; *A.*, i, 749.

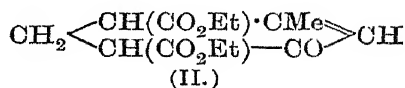
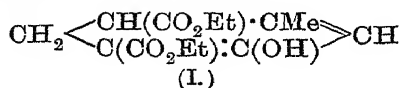


The thirty-nine types are classified by him according to the number of changes of linking involved, and, further, into those which respectively do and do not involve change of valency. The scheme affords a useful review of the labile types of isomerism.

The equilibrium between ketonic and enolic modifications has been studied from many points of view. Michael, in a theoretical review of the whole subject,<sup>68</sup> insists on the necessity of distinguishing clearly between desmotropy, the reversible transformation of two isomerides into each other through the wandering of a labile hydrogen atom, and mesotropy, the process of irreversible isomerisation during the formation of derivatives. In subsequent papers, he and others have investigated the suitability of various reagents for distinguishing between enolic and ketonic substances. The best modification of Hantzsch's ammonia reaction consists in employing triethylamine or tripropylamine, and in noting the development of heat rather than the formation of a precipitate.<sup>69</sup> This is quite satisfactory when the compound is mesotropic, only enolic substances then reacting, but desmotropic compounds are, as might be expected, generally converted into the more stable modification by the amine. The results obtained with phenylcarbimide<sup>70</sup> and with acetyl chloride or acetic anhydride<sup>71</sup> are also indecisive in such cases, for similar reasons.

Ethyl oxalosuccinonitrile,  $\text{CN} \cdot \text{CH}_2 \cdot \text{CH}(\text{CN}) \cdot \text{CO} \cdot \text{CO}_2\text{Et}$ , prepared by condensing ethyl oxalate with succinonitrile, has been obtained<sup>72</sup> in an enolic and a ketonic modification, both of which are crystalline. The latter form dissolves alcohol in to a violet, fluorescent solution. If confirmed, this would be the first case of fluorescence observed in the aliphatic series, and Kauffmann has therefore suggested the presence of a ring; the chemical reactions, however, indicate that the compound has the simple structure assigned to it.

The enolic (I) and ketonic (II) modifications of ethyl methylcyclohexenonedicarboxylate:



are stated<sup>73</sup> to give different vapours when distilled, although both modifications have the same boiling point. Desmotropy has not previously been observed to persist in the state of vapour.

<sup>68</sup> A. Michael, *Annalen*, 1908, **363**, 20; *A.*, i, 943.

<sup>69</sup> A. Michael and H. D. Smith, *ibid.*, 36; *A.*, i, 943.

<sup>70</sup> A. Michael and P. H. Cobb, *ibid.*, 64; *A.*, i, 947.

<sup>71</sup> A. Michael and A. Murphy, jun., *ibid.*, 94; *A.*, i, 949.

<sup>72</sup> W. Wislicenus and P. Berg, *Ber.*, 1908, **41**, 3757; *A.*, i, 965.

<sup>73</sup> P. Rabe, *Annalen*, 1908, **360**, 289; *A.*, i, 530.

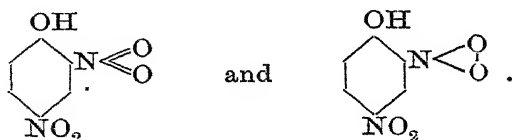
9-Nitrofluorene has been isolated in two desmotropic forms, of which the *aci*-form,  $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{C}:\text{NO}\cdot\text{OH}$ , is comparatively stable. It is prepared from fluorene, ethyl nitrite, and potassium ethoxide.<sup>74</sup>

The well-known tautomerism of cyclic ketones, such as phloroglucinol and dihydroresorcinol, is also exhibited by monoketones containing a simple ring if a sufficiently powerful reagent, such as an acid anhydride, be employed to detect the enolic hydroxyl group.<sup>75</sup> In this way, acetyl derivatives of the enolic forms of *cyclohexanone* and its three methyl derivatives, and of *menthone*, *cyclopentanone*, and *suberone*, have been prepared. Camphor gave no indication of any acetylation.

An addition to the many physical properties which have been utilised to give indications as to the ketonic or enolic condition of tautomeric substances is made in a recent communication, which deals with the viscosity of liquids of this class, these compounds being mixed with various solvents.<sup>76</sup> The measurements show that ethyl acetoacetate is partly enolised, both alone and in solution. The addition of piperidine has a marked effect in increasing the viscosity.

The peculiar isomerism of di-*o*-derivatives of benzene, referred to in last year's Report (p. 111), and there considered in relation to Kekulé's formula for benzene, has received surprisingly little attention, and it is therefore uncertain how far the formation of such isomerides is a general one. A certain number of nitrated derivatives of benzene, it is true, have been shown to exist in two modifications, but this is now attributed by the author<sup>77</sup> to isomerism of the nitro-group. Thus 1-chloro-2:4-dinitrobenzene exists in a stable and in a highly labile form, the two forms being chemically identical. The fact that both modifications have the same colour excludes the possibility that one of them has the *aci*-constitution.

The two modifications of 2:4-dinitrophenol, however, differ in colour, one of them being pale green in solution or when fused. The two substances give a eutectic mixture, they form similar salts, and are formulated as :



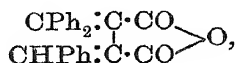
<sup>74</sup> W. Wislicenus and M. Waldmüller, *Ber.*, 1908, **41**, 3334; *A.*, i, 973.

<sup>75</sup> C. Mannich and V. H. Hâncu, *ibid.*, 1908, **41**, 564; *A.*, i, 275.

<sup>76</sup> A. E. Dunstan and J. A. Stubbs, *Trans.*, 1908, **93**, 1919.

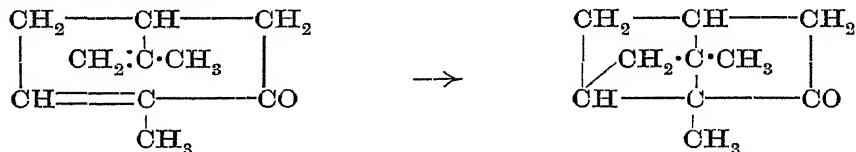
<sup>77</sup> I. Ostromisslensky, *J. pr. Chem.*, 1908, [ii], **78**, 263; *A.*, i, 868.

The very remarkable changes undergone by the aromatic fulgides, of which triphenylfulgide,

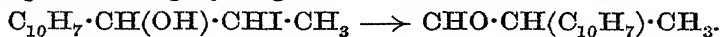


is a type, when exposed to light have been fully studied.<sup>78</sup> The change from orange to brown, brought about by light, is strictly reversible, but after frequent repetition of the change, an irreversible transformation occurs, resulting in the formation of "photo-anhydrides," the investigation of which has not yet been published. A theoretical discussion is at present hardly possible, but it may be noted that the triarylated fulgides (with one exception) and certain of those containing two aryl groups are phototropic, whereas tetraphenylfulgide is not. Certain compounds outside this group behave in a similar manner.

An isomeric change of a more definite character, also taking place under the influence of light, is that of carvone.<sup>79</sup> Whilst solutions of dihydrocarvone were hydrolysed by exposure to sunlight, thus behaving similarly to other cyclic ketones, carvone was converted into an isomeride, resisting the action of permanganate. It is suggested that a process of "internal polymerisation," such as that represented below, takes place:



The migration of acyl groups in certain instances will be discussed later in connexion with the structure of hydroxyazo-compounds. The migration of aryl groups in iodohydrins during the elimination of hydrogen iodide has been exhaustively studied.<sup>80</sup> Thus  $\alpha$ -1-naphthylpropylene,  $\text{C}_{10}\text{H}_7 \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_3$ , on treatment with mercuric oxide and iodine, is transformed into  $\alpha$ -1-naphthylpropaldehyde, the iodohydrin isomerising and losing hydrogen iodide at the same time:



Similarly,  $\beta$ -1-naphthylpropylene passes into  $\alpha$ -naphthylacetone:



A case of wandering of bromine has been observed in the transformation of nitroamines.<sup>81</sup> 2:6-Dibromo-1-nitroaminobenzene under-

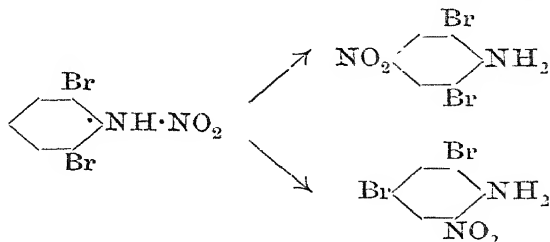
<sup>78</sup> H. Stobbe, *Annalen*, 1908, **359**, 1; *A.*, ii, 339.

<sup>79</sup> G. Ciamician and P. Silber, *Ber.*, 1908, **41**, 1928; *A.*, i, 555.

<sup>80</sup> M. Tiffeneau, *Bull. Soc. chim.*, 1907, [iv], **1**, 1205; *Compt. rend.*, 1908, **146**, 29; **147**, 678; *A.*, i, 165, 166, 972.

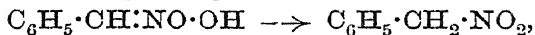
<sup>81</sup> K. J. P. Orton and C. Pearson, *Trans.*, 1908, **93**, 725.

goes rearrangement in the usual way to 2:6-dibromo-4-nitroaniline, but at the same time a part of it forms the isomeric 2:4-dibromo-6-nitroaniline, the migrating nitro-group actually expelling a bromine atom, which re-enters the nucleus in a different position :



With *s*-tribromo-1-nitroaminobenzene, the same change takes place, but the para-position now being occupied, the bromine is unable to re-enter the nucleus, and is found in the solution.

In concluding this section, reference should be made to the interesting method of studying the process of isomeric change by observing the change in rotatory power of an active solvent, not itself undergoing change, as described in last year's Report (p. 184). The method is particularly applicable to the oximes, and one case has been investigated, that of *p*-iodobenz-*syn*.-aldoxime, in which no other method for measuring the velocity of change is available. The change in rotation of *n*-propyl tartrate brought about by the presence of *ω*-*iso*-nitromethane undergoing change to the stable nitro-compound :



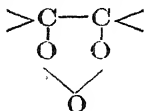
is less than that due to the oximes, but is still considerable. The change of ammonium cyanate and thiocyanate into carbamide and thiocarbamide respectively may be followed by dissolving a portion of the substance which is being heated from time to time in an aqueous solution of ethyl tartrate and measuring the rotation, or in the former case, by allowing the change to take place in the ethyl tartrate solution.<sup>82</sup>

#### Ozonides.

The value of the ozone method for recognising the presence of ethylenic linkings continues to be disputed. Whilst Molinari states that such linkings only are attacked by ozone, Harries finds that substances containing triple linkings also react readily with ozone to form unstable products having the properties of ozonides. It is suggested that the differences observed may be due to the fact that Molinari employs ozonised air, and Harries, the presumably more energetic ozonised oxygen. The simpler olefines yield very stable ozonides, which may be distilled in a vacuum, when treated with ozone in an

<sup>82</sup> T. S. Patterson and A. McMillan, *Trans.*, 1908, 93, 1041.

indifferent solvent.<sup>83</sup> The formulation of such compounds as containing a chain of three oxygen atoms :



is not in accordance with their optical constants, and it appears rather that only two of the oxygen atoms have an ether linking, the third being "carbonyl oxygen," but further study is required before a definite formula can be assigned to them. The decomposition products of ozonides of oleic acid and triolein by water and alkalis are very complex, although the "saponification number" of such compounds is a fairly definite constant.<sup>84</sup>

#### *Aliphatic Diazo- and Triazo-compounds.*

In 1907 an investigation of the action of sodium azide on various diazonium salts led to the production of a number of aromatic azides, of which the most noteworthy were the hydroxyphenylazoimides, obtained from the aminophenols, and the triazo-derivatives of the naphthalene series, prepared from the isomeric nitronaphthalene-diazonium salts.<sup>85</sup>

An extension of this research to the aliphatic series has resulted in the isolation of triazo-derivatives of the simplest organic compounds. By double decomposition, ethyl chloroacetate and sodium azide have furnished ethyl triazoacetate,  $N_3 \cdot CH_2 \cdot CO_2Et$ , from which triazoacetic acid,  $N_3 \cdot CH_2 \cdot CO_2H$ , and triazoacetamide,  $N_3 \cdot CH_2 \cdot CO \cdot NH_2$ , have been prepared by the usual methods. The simplest triazo-ketone, acetonylazoimide, or triazoacetone,  $N_3 \cdot CH_2 \cdot CO \cdot CH_3$ , has been obtained, and compared with its cyclic analogue, camphorylazoimide. Triazoacetoxime has been isolated, and the isomeric ethyl  $\alpha$ - and  $\beta$ -triazopropionates have been prepared, but only the former ester could be hydrolysed into  $\alpha$ -triazopropionic acid,  $CH_3 \cdot CH(N_3) \cdot CO_2H$ , the  $\beta$ -ester being decomposed by caustic alkalis, and even by ammonia, with the elimination of the triazo-group. Triazoethyl alcohol,  $N_3 \cdot CH_2 \cdot CH_2OH$ , and triazoacetaldehyde,  $N_3 \cdot CH_2 \cdot COH$ , were obtained from ethylene chlorohydrin and chloroacetaldehyde; the former was a fairly stable substance, giving rise to esters, such as triazoethyl acetate,



isomeric with ethyl triazoacetate, and the latter was an extremely explosive and unstable liquid, which was decomposed by hydroxylamine, phenylhydrazine, and other reagents for aldehydes.

<sup>83</sup> C. D. Harries and K. Haefner, *Ber.*, 1908, **41**, 3098; *A.*, i, 846.

<sup>84</sup> E. Molinari, *ibid.*, 585, 2782, 2789, 2794; *A.*, i, 244, 849.

<sup>85</sup> M. O. Forster and H. E. Fierz, *Trans.*, 1907, **91**, 855, 1350, 1942.

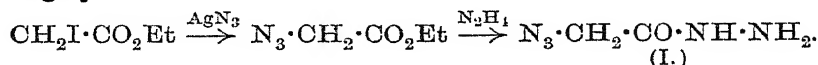
The refraction and dispersion of certain of these triazo-compounds were determined, so also were the dissociation constants of triazoacetic and  $\alpha$ -triazopropionic acids, the latter determinations showing that the effect on the strength of acetic acid produced by the introduction of a triazo-group is less than that due to a bromine atom but greater than that due to an iodine atom.<sup>86</sup>

Bistriazo-compounds were also prepared: 1:2-bistriazoethane,  $\text{N}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{N}_3$ , and ethyl bistriazoacetate,  $\text{CH}(\text{N}_3)_2\cdot\text{CO}_2\cdot\text{C}_2\text{H}_5$ , the latter being distilled and analysed in spite of its explosive properties. 1:1-Bistriazoethane,  $\text{CH}_3\cdot\text{CH}(\text{N}_3)_2$ , which was produced by the general method from ethylidene dichloride and sodium azide, could not be distilled even under greatly reduced pressure, owing to the violence with which it explodes at temperatures below  $50^\circ$ .

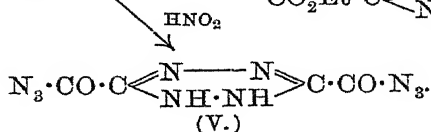
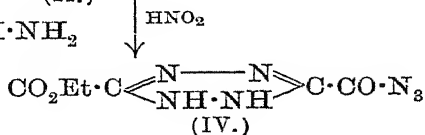
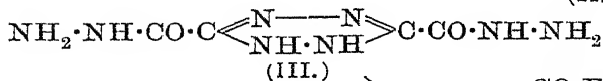
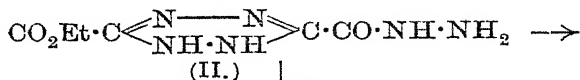
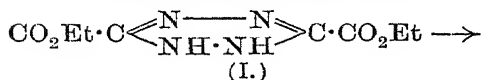
$\alpha$ -Triazopropionic acid, which is a racemic compound, was resolved by means of brucine, and the laevorotatory component reduced to *D*-alanine.<sup>87</sup>

Ethyl diazoacetate, first discovered by Curtius, gives rise to a complicated series of transformation products under the influence of alkalis. A tabulated summary of some of these derivatives was given in last year's Report (p. 158). Among the points studied since this table was published is the action of hydrazine on ethyl diazoacetate and bisdiazooacetate and their imides.

Triazoacetylhydrazide (I) is produced either by the action of hydrazine hydrate on diazoacetamide or by treating ethyl diazoacetate with anhydrous hydrazine; its constitution is demonstrated by the following synthesis:



The six-membered dihydrotetrazine ring in ethyl bisdiazooacetate (I),



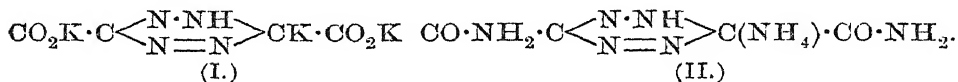
<sup>86</sup> J. C. Philip, *Trans.*, 1908, **93**, 918, 925.

<sup>87</sup> M. O. Forster and H. E. Fierz, *ibid.*, 72, 669, 1070, 1174, 1859, 1865.

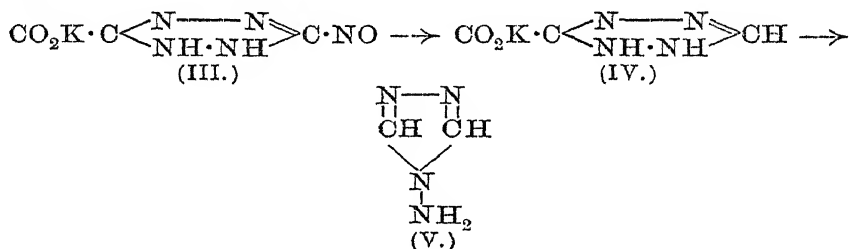
is not affected by hydrazine, the action of which is effective only on the carbethoxy-groups, thus giving rise to ethyl bisdiazacetate hydrazide (II) and bisdiazacetic acid dihydrazide (III).

These hydrazides are converted respectively by nitrous acid into ethyl tetrazinedicarboxylate azide (IV) and tetrazinedicarboxyl bisazide (V).<sup>88</sup>

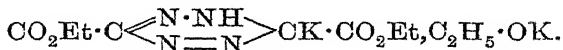
The action of cold concentrated aqueous potassium hydroxide on ethyl diazoacetate leads to the production of tripotassium  $\psi$ -diazacetate (I), a compound which is transformed by this alkali at 100° into potassium bisdiazacetate:



This tripotassium salt corresponds with the amide (II) produced by the action of liquid ammonia on ethyl diazoacetate. On treatment with alkali nitrite and acetic acid, this potassium salt yields potassium nitro-dihydrotetrazinecarboxylate (III), from which reduction with hydrogen sulphide leads to dihydrotetrazinecarboxylic acid (IV), a substance which, even at 60°, loses carbon dioxide and passes into *N*-1-amino-1:3:4-triazole (V).<sup>89</sup>



The compound obtained by the action of potassium ethoxide on ethyl diazoacetate is not, as was formerly supposed by Hantzsch and Lehmann,<sup>90</sup> a potassium ethyl isodiazacetate,  $\text{CO}_2\text{Et} \cdot \text{C} \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \text{K} \end{array}$ , but a  $\psi$ -diazacetate derivative (potassium ethyl  $\psi$ -diazacetate) containing a molecule of potassium ethoxide:



The corresponding sodium derivative is known, and both substances have all the properties of  $\psi$ -diazacetates (*CN*-dihydro-1:2:4:5-tetrazine-3:6-dicarboxylates).<sup>91</sup>

<sup>88</sup> T. Curtius and E. Rimele, *Ber.*, 1908, **41**, 3108; *A.*, i, 921.

<sup>89</sup> Ernst Muller, *ibid.*, 3116; *A.*, i, 922.

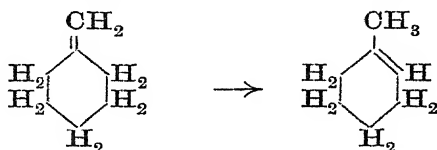
<sup>90</sup> *Ber.*, 1901, **34**, 2506; *A.*, 1901, i, 678.

<sup>91</sup> T. Curtius, A. Darapsky, and Ernst Muller, *ibid.*, 1908 **41**, 3140; *A.*, i, 923.

Further details of the transformations of ethyl diazoacetate will be found in a recently-published résumé of the work.<sup>92</sup>

### *The Terpene Group.*

Great activity has been shown in the investigation of the terpenes and allied substances during the past year, and important progress has been made in the establishment of the constitution of several members of the group. The great services rendered to this branch of chemistry, as to so many others, by the discovery of Grignard's reaction are obvious on an examination of the papers dealing with terpene syntheses. It is in connexion with the study of the terpenes, also, that the optical method, the determination of the refractive index and dispersion, has proved of the greatest value. Several cases of apparent exception to the regularities in the relation of refractive index to constitution have been removed recently, as the result of a more complete purification of the substances supposed to be anomalous. There still remain some marked apparent exceptions, some of which may be due to unnoticed isomerisation during the preparation. Such isomeric changes, usually involving the shift of a double linking, are frequent. In a recent instance, the process of heating with quinoline and quinoline hydriodide, a procedure sometimes adopted, is found to cause the rearrangement of methylenecyclohexane to methyl- $\Delta^1$ -cyclohexene, the double linking changing its position :<sup>93</sup>



The synthesis of carvestrene<sup>94</sup> has now been supplemented by the synthesis of an isomeride, also of the *m*-menthadiene series, for which the name *isocarvestrene* is proposed, the two terpenes differing only in the position of the double bond in the ring.<sup>95</sup> Starting with ethyl cyclohexanone-2 : 4-dicarboxylate (I), methylation gives ethyl 1-methylcyclohexan-6-one-1 : 3-dicarboxylate (II), which loses a carbethoxyl group on hydrolysis, yielding 1-methylcyclohexan-6-one-3-carboxylic acid (III).

By reduction to the hydroxy-acid, treatment with hydrogen bromide, and subsequent removal of hydrogen bromide by diethylaniline, an

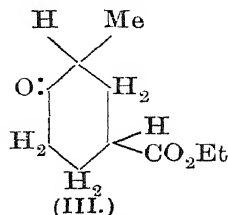
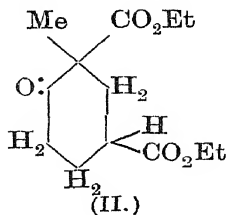
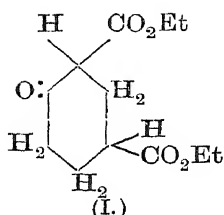
<sup>92</sup> *Ber.*, 1908, **41**, 3161 ; *A.*, i, 924.

<sup>93</sup> A. E. Faworsky and I. Borgmann, *Ber.*, 1907, **40**, 4863 ; *A.*, i, 15.

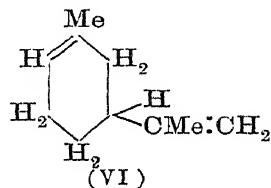
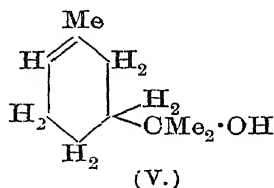
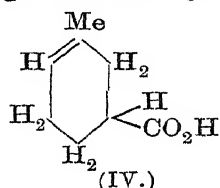
<sup>94</sup> *Ann. Report*, 1907, 129.

<sup>95</sup> K. Fisher and W. H. Perkin, jun., *Trans.*, 1908, **93**, 1876.



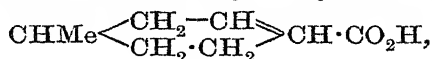


acid is obtained which is shown to be 1-methyl- $\Delta^6$ -cyclohexene-3-carboxylic acid (IV). Magnesium methyl iodide converts the unsaturated acid into  $\Delta^6$ -*m*-menthenol (V), the terpeneol of the series, from which *isocarvestrene* (VI) is obtained by removing water with magnesium methyl iodide.



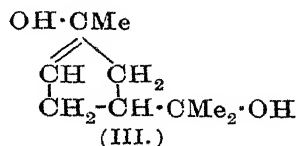
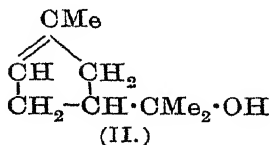
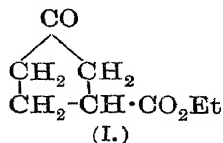
The new terpene is found to possess somewhat remarkable properties, the high refraction and dispersion, and the formation of a dibromide instead of a tetrabromide, causing it to resemble a terpene with conjugated double linkings, a constitution which appears to be excluded by the conditions of the synthesis.

The important synthesis of terpeneol by W. H. Perkin, jun., in 1904,<sup>96</sup> has been completed by the production of the two active terpeneols, the original product having been inactive. This has been effected by the resolution of *dl*-1-methyl- $\Delta^3$ -cyclohexene-4-carboxylic acid,



by crystallisation of its strychnine and brucine salts.<sup>97</sup>

Another interesting synthesis from the same laboratory has been that of a terpeneol, terpin, and terpene containing a five-membered ring.<sup>98</sup> Ethyl cyclopentanone-3-carboxylate (I) reacts with magnesium methyl iodide, forming 1-methyl-3-isopropenol- $\Delta^5$ -cyclopentene (II) the terpeneol of the five-carbon series, which yields the corresponding terpin (III) with acids:

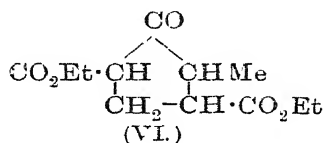
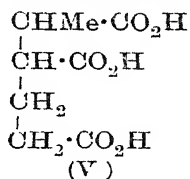
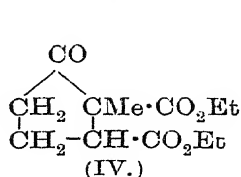


<sup>96</sup> *Ann. Report*, 1904, 116.

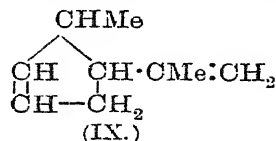
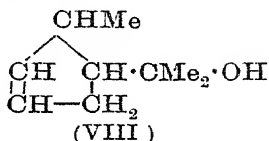
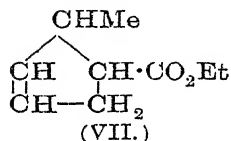
<sup>97</sup> K. Fisher and W. H. Perkin, jun., *Trans.*, 1908, **93**, 1871.

<sup>98</sup> W. N. Haworth and W. H. Perkin, jun., *Trans.*, 1908, **93**, 573.

A second method of synthesis leads equally to members of this series. Ethyl 2-methylcyclopentan-2-one-3-dicarboxylate (IV) may be broken down by hydrolysis to pentane- $\beta\gamma$ -tricarboxylic acid (V), the ethyl ester of which condenses under the influence of sodium, forming ethyl 2-methylcyclopentanone-3:5-dicarboxylate (VI). By reduction and addition and subsequent removal of hydrogen bromide, a

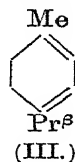
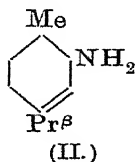
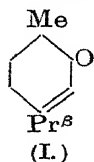


mixture of unsaturated esters is obtained, from which ethyl 1-methyl- $\Delta^4$ -cyclopentene-2-carboxylate (VII) has been isolated by an ingenious process. Magnesium methyl iodide converts it into the terpeneol (VIII). The corresponding terpene, 1-methyl-2-isopropenyl- $\Delta^4$ -cyclopentene



(IX) is obtained from this by dehydration with succinic anhydride. This hydrocarbon is possibly identical with that obtained by Semmler from sabina ketone.

It is only possible to make a selection from the very numerous papers dealing with terpene chemistry. Terpinene, although rarely present in natural products, is of interest from the fact that it is frequently produced by the action of acids on other terpenes, and therefore appears to be one of the most stable members of the group. It has been previously suggested that terpinene is identical with carvenene, and this is confirmed by the conversion of carvenone (I) by way of the oxime into 2-amino- $\Delta^3$ -menthene (II), distillation of the phosphate of the latter yields a pure  $\Delta^{1:3}$ -menthadiene (carvenene) (III), which, from its conversion into terpinene nitrosite, appears to be identical with terpinene.<sup>99</sup> Whilst former preparations of terpinene



have failed to show the optical exaltation corresponding with the con-

<sup>99</sup> C. D. Harries and R. Majima, *Ber.*, 1908, 41, 2516; *A.*, i, 733.

jugated double linkings, it is exhibited by the carvenene prepared by this method.<sup>1</sup> A study of the oxidation products of  $\alpha$ - and  $\beta$ -terpinene also leads to the conclusion that the hydrocarbon yielding the nitrosite is  $\Delta^{1:3}$ -menthadiene ( $\alpha$ -terpinene).<sup>2</sup>

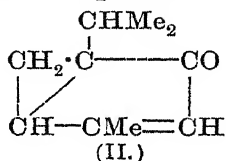
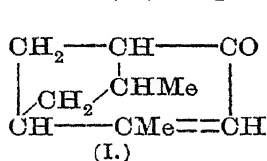
The new terpene obtained from Cyprus origanum oil, and described as organene, has also the properties of  $\Delta^{1:3}$ -*p*-menthadiene, and shows optical exaltation. Its properties agree fairly well with those of carvenene or  $\alpha$ -terpinene.<sup>3</sup>

2-Methylcarvenene has been prepared by the action of magnesium methyl iodide on carvenone.<sup>4</sup>

The first synthesis of  $\alpha$ -phellandrene from a substance containing a smaller number of carbon atoms has been accomplished by treating isopropyl- $\Delta^2$ -cyclohexen-4-one, prepared by the isomerisation of sabina ketone, with magnesium methyl iodide.<sup>5</sup>

Turning now to bicyclic terpenes, a comparative study of the action of hydration in breaking down bridged linkings has been made by Wallach.<sup>6</sup> The addition is very commonly accompanied by molecular rearrangement, sabinene and pinene hydrates, for instance, probably first losing water, which is then added on in a different position, yielding terpinene-4-ol and  $\alpha$ -terpineol respectively. The relative behaviour of three- and four-atom rings on hydration confirms Perkin's conclusion, derived from experiments of a different kind, that the relative stability of cyclopropane and cyclobutane rings depends much more on the nature and position of the attached groups than on the number of carbon atoms in the ring.

Of the two possible formulæ for umbellulone<sup>7</sup> proposed by Tutin (I) and by Semmler (II) respectively, the first is preferred, since the



second would require that tetrahydroumbellulone should be menthone, whereas the mixture of stereoisomeric tetrahydro-derivatives actually obtained is unlike menthone.

<sup>1</sup> J. W. Bruhl, *Ber.*, 1908, **41**, 3712; *A.*, ii, 1002.

<sup>2</sup> O. Wallach, *Annalen*, 1908, **362**, 261, 285; *A.*, i, 811, 813; Semmler, however (*Ber.*, 1908, **41**, 4474; *A.*, 1909, i, 110), dissents from this conclusion, and maintains the  $\Delta^{1:4}$  constitution for terpinene.

<sup>3</sup> S. S. Pickles, *Trans.*, 1908, **93**, 862.

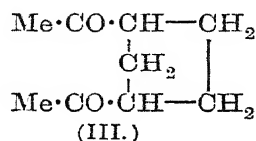
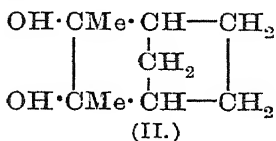
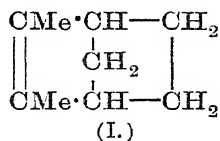
<sup>4</sup> H. Rupe and F. Emmerich *Ber.*, 1908, **41**, 1750; *A.*, i, 556.

<sup>5</sup> O. Wallach, *Annalen*, 1908, **359**, 265; *A.*, i, 424.

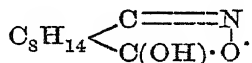
<sup>6</sup> *Annalen*, 1908, **360**, 82; *A.*, i, 429.

<sup>7</sup> F. Tutin, *Trans.*, 1908, **93**, 252; F. W. Semmler, *Ber.*, 1908, **41**, 3988; *A.*, 1909, i, 38.

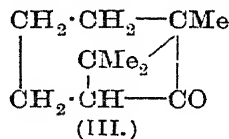
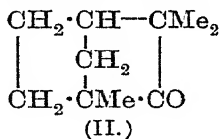
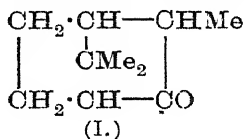
Santene has received the constitution (I) on the ground that gentle oxidation with permanganate yields a glycol (II), further oxidation giving a diketone (III), the constitution of which is proved by its oxidation to *trans*-yclopentanedicarboxylic acid.<sup>8</sup>



A further attempt has been made to elucidate the nature of the isomerism of the two modifications of *isonitrosocamphor* by the study of the action of diazomethane.<sup>9</sup> This reagent converts the unstable into the stable modification, and the latter into the *N*-ether, which is possibly  $\text{C}_8\text{H}_{14} \begin{smallmatrix} \text{O} \cdot \text{NMe} \cdot \text{O} \\ \diagup \quad \diagdown \\ \text{C} \end{smallmatrix}$ . The presence of a nitroso-group is improbable, from the absence of a blue or green colour and of the Liebermann reaction, and the production of the *N*-ether is in better agreement with the formulation of *isonitrosocamphor* as

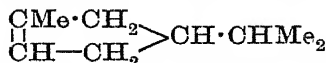


Several investigations have been directed to the establishment of the constitution of fenchone. Three formulæ have been proposed, due respectively to Wallach (I), Semmler (II), and Glover (III). Of these,



the first formula is very similar to that of  $\alpha$ -methylcamphor, and the second to that of  $\alpha\alpha$ -dimethylcamphor. Both are open to the objection that fenchone behaves very differently from camphor in many of its reactions. The oxidation of fenchene and fenchone<sup>10</sup> leads to indecisive results, it being difficult to reconcile the reactions observed with either of the proposed formulæ. The production of dihydrofencholenamide,

$\text{NH}_2 \cdot \text{CO} \cdot \text{CMe} \cdot \text{CH}_2 \begin{smallmatrix} \text{CH} \cdot \text{CHMe}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix}$ , by the action of sodamide on fenchone, and the formation of *apofenchene*,



(the constitution of which is established by its oxidation through a

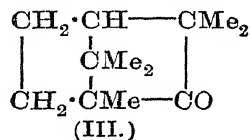
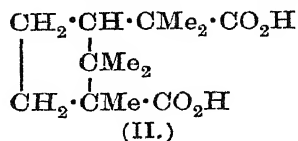
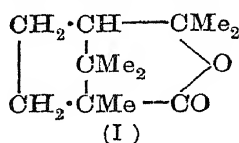
<sup>8</sup> F. W. Semmler and K. Bartelt, *Ber.*, 1908, **41**, 385, 866; *A.*, i, 195, 355.

<sup>9</sup> M. O. Forster and H. Holmes, *Trans.*, 1908, **93**, 242.

<sup>10</sup> O. Wallach, *Annalen*, 1908, **362**, 174; *A.*, i, 809.

ketonic acid to  $\beta$ -isopropylglutaric acid) from the latter, is considered <sup>11</sup> to favour Semmler's formula.

$\alpha\alpha$ -Dimethylcamphor (III) should be capable of preparation from dimethylcampholide (I) by addition of potassium cyanide, hydrolysis to dimethylhomocamphoric acid (II), and distillation of the calcium salt. A comparison of this compound with fenchone should then be of considerable interest. It was found, however,<sup>12</sup> that although the



required dimethylcampholide was readily obtained by the action of magnesium methyl iodide on camphoric anhydride, it was impossible to cause combination with potassium cyanide, isomerisation to an unsaturated acid always taking place.

The preparation of a number of derivatives of  $\alpha$ -methylcamphor has shown <sup>13</sup> that this compound is entirely similar to camphor, and consequently unlike fenchone.  $\alpha$ -Methylcamphor forms bromo- and sulpho-derivatives closely resembling those of camphor.

The synthesis of an isomeride of  $\beta$ -pinene from nopinone, described in last year's Report (p. 132), has been modified, and decomposition of the unsaturated acid is now found to yield fenchene or  $\beta$ -pinene, according to the conditions of dehydration of the nopinolacetic acid. The fenchene is probably formed by intramolecular change of  $\beta$ -pinene. Since  $\beta$ -pinene yields bornyl chloride with hydrogen chloride, both camphor and camphene may be prepared from it, this being the first synthesis of camphor from a compound (nopinone) containing a smaller number of carbon atoms.<sup>14</sup>

A cyclooctadiene was obtained by Willstätter and Veraguth in 1905 from the alkaloid  $\psi$ -pelletierine, and its ready polymerisation suggested the presence of conjugated double linkings in the molecule.<sup>15</sup> This compound derives its principal interest from the fact that caoutchouc is supposed to be a polymerised dimethyl derivative of the same hydrocarbon. Since, however, the  $\Delta^{1,5}$ -members of this series also polymerise readily, this constitution also becomes a possible one. An examination of the diozonide, which is hydrolysed by water to succindialdehyde, proves that the double linkings are in the 1 : 5-position : <sup>16</sup>

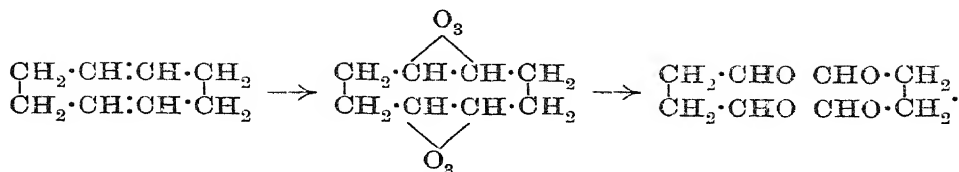
<sup>11</sup> L. Bouveault and Levallois, *Compt. rend.*, 1908, **146**, 180 ; *A.*, i, 193.

<sup>12</sup> G. Komppa, *Ber.*, 1908, **41**, 1039 ; *A.*, i, 352.

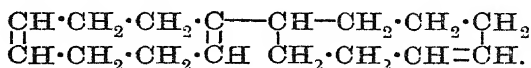
<sup>13</sup> W. H. Glover, *Trans.*, 1908, **93**, 128f.

<sup>14</sup> O. Wallach, *Annalen*, 1908, **363**, 1 ; *A.*, i, 997.

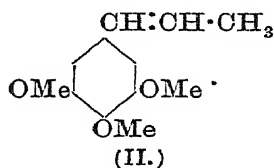
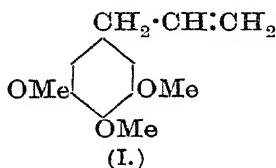
<sup>15</sup> *Ann. Report*, 1905, 121. <sup>16</sup> C. D. Harries, *Ber.*, 1908, **41**, 671 ; *A.*, i, 254.



The investigation of the polymerisation products showed that there was no direct connexion between the constitution of the hydrocarbon and that of caoutchouc. The simplest polymeride, *dicyclooctadiene*, appears from its behaviour with ozone to have the constitution :



Connected with the ethereal oils, although not a member of the terpene group, is *elemicin*, isolated by Semmler from *elemi resin*.<sup>17</sup> This is proved to be 3:4:5-trimethoxy-1-allylbenzene (I). When distilled over sodium, it is converted into the isomeric propenyl

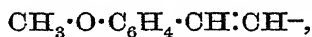


derivative, *isoelemicin* (II). Permanganate oxidises it to 3:4:5-trimethoxybenzoic acid. Sodium and alcohol reduce both *elemicin* and *isoelemicin* to 3:5-dimethoxy-1-*n*-propylbenzene, the *p*-methoxyl group being eliminated.

### *Crystalline Liquids.*

The property of existing in a liquid phase, which exhibits certain of the optical properties of crystalline solids, for example, double refraction, is possessed by many organic substances, and the relationship which in all probability exists between their chemical constitution and the development of this crystalline liquid condition is at present under investigation.

In *p*-methoxycinnamic acid, which exhibits this peculiarity, the property is probably due to the presence of the group



for *dianisyltetraphenylene*, which consists of two of these radicles, still retains the power of forming an anisotropic liquid. *p*-Methylaminobenzaldehydephenylhydrazone,  $\text{CH}_3 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_5$ , *s*-di-

<sup>17</sup> F. W. Semmler, *Ber.*, 1908, **41**, 1768, 1918, 2183, 2556; *A*, i, 557, 558, 664, 734.

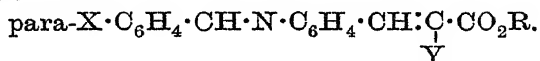
ethylbenzidine,  $\text{C}_2\text{H}_5\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_2\text{H}_5$ , and *p*-methoxycinnamaldazine,

$\text{CH}_3\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{N}\cdot\text{N}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_3$ , which likewise display this phenomenon, are either para-substituted compounds or possess long, straight chains.<sup>18</sup> Cholesterol derivatives, which frequently exhibit the crystalline liquid condition, probably contain an asymmetric group and a long, straight chain.

The turbidity of many of these crystalline liquids is not due to suspended impurities, emulsions, or inclusions of foreign substances, but is a natural consequence of the presence of differently situated anisotropic, crystalline fragments. Moreover, perfectly clear crystalline liquids have now been prepared, some of which maintain their transparency in any position, whilst others are clear or turbid according to the incidence of the light.

The chemical constitution of substances forming crystalline liquid phases warrants the view that a linear structure favours the development of the property, whilst a cruciform or many-branched configuration inhibits this condition.

Para-substituted benzylidene-*p*-amino- $\alpha$ -alkylcinnamates having the following general formula have been prepared and examined from this standpoint :



The tendency to develop the crystalline liquid condition reaches its maximum when an ethyl or a *n*-propyl group is introduced at R (the ester radicle) ; it is also increased by the replacement of methoxyl at X (the para-substituent) by ethoxyl or phenyl. The lengthening of the side-chain Y in the order methyl, ethyl, and phenyl inhibits to an increasing extent the property of exhibiting the liquid crystalline condition. The property of circular polarisation is developed to a remarkable extent by the introduction of an active amyl group into position R.

The ethyl *p*-azoalkylcinnamates and *p*-azoxyalkylcinnamates resemble the foregoing azomethine derivatives in respect of this property of assuming the crystalline liquid condition.<sup>19</sup>

The simpler azoxy-derivatives (azoxybenzene, *p*-azoxyphenetole, the three isomeric azoxytoluenes, and azoxyanisoles) can also exist in the anisotropic liquid condition, and it is stated that these modifications differ from the ordinary varieties in certain chemical properties. Among other anomalous reactions, they give the Liebermann nitroso-coloration, and are not transformed into hydroxyazo-compounds.<sup>20</sup>

<sup>18</sup> T. Rotarski, *Ber.*, 1908, **41**, 1994 ; *A.*, i, 640.

<sup>19</sup> D. Vorlander, *ibid.*, 2033 ; *A.*, i, 641.

<sup>20</sup> T. Rotarski, *ibid.*, 865 ; *A.*, i, 374.

These differences are sufficiently remarkable to warrant a more extended investigation.

### *Optical Activity.*

In recent measurements of the optical activity of organic compounds, the theoretical connexion with the degree of asymmetry of the molecule, as expressed by Guye's "asymmetry product,"<sup>21</sup> has been frequently referred to and discussed, without, however, any very definite conclusions having been yet reached. A recent physical investigation<sup>22</sup> leads to the conclusion that the variation in the value of the expression with the temperature and the wave-length of the light used must be taken into account. The author states that if a substance containing a single asymmetric carbon atom could be found, the temperature of reversal of sign of which could be determined, a means would be provided of testing the validity of the modified Guye's equation, but this test has not yet been applied.

The difficulty of finding any simple formula for the relation has been further illustrated by the examination of a series of salts, all of which contained *p*-bromophenyl, methyl, and allyl, the remaining group being ethyl, *n*-propyl, isopropyl, or isoamyl. As in similar series examined previously, no simple relation was discovered.<sup>23</sup> The influence of the constitution of the substituting groups may also be so great as to outweigh that of mass.<sup>24</sup>

The influence of the introduction of unsaturated groups into the molecule has also been further studied.<sup>25</sup> The alkaloid salts of a number of acids were examined, and the rule that the change from the saturated to the ethylenic linking produces an increase in the rotatory power was confirmed. The triple linking, however, may give rise to a higher or a lower value in different cases, the direction depending mainly on the asymmetric part of the molecule. Neither could any rule be found for the comparative influence of *cis*- and *trans*-configurations. The presence of several unsaturated groups still further increases the optical activity, the relative nearness of the unsaturated linkings having an important effect. The investigation was extended to include sulphur derivatives in which the valency of the sulphur, and therefore the amount of its residual affinity, was variable. The progressively increasing unsaturation of the sulphur in the sulphone,  $R_2SO_2$ , the sulfoxide,  $R_2SO$ , and the sulphide,  $R_2S$ , is accompanied by a small increase in the rotation, but the conjugation

<sup>21</sup> *Ann. Report*, 1907, 178.

<sup>22</sup> E. Bose, *Physikal. Zeitsch.*, 1908, 9, 860; *A.*, 1909, ii, 2.

<sup>23</sup> H. O. Jones and J. R. Hill, *Trans.*, 1908, 93, 295.

<sup>24</sup> R. W. Everatt, *ibid.*, 1225, 1789.

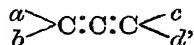
<sup>25</sup> T. P. Hilditch, *ibid.*, 700, 1388, 1618.



of two bivalent sulphur atoms in the disulphide,  $RS \cdot SR$ , produces a relatively enormous effect. The results obtained with alkaloid salts of aromatic sulphonic and sulphinic acids follow the same rule if the latter are assumed to contain sexavalent, and not quadrivalent, sulphur, an assumption for which there is chemical evidence. If both series of compounds contain sexavalent sulphur, the sulphonic acids will be the less saturated, owing to hydroxyl, possessing some residual affinity, replacing hydrogen:  $R \cdot SO_2 \cdot H \rightarrow R \cdot SO_2 \cdot OH$ .

No certain occurrence of optical activity has yet been observed in a compound in which the asymmetric carbon atom is not attached to other carbon atoms. Two compounds of very simple structure, chlorosulphoacetic acid,  $SO_3H \cdot CHCl \cdot CO_2H$ , and chlorobromomethanesulphonic acid,  $CHClBr \cdot SO_3H$ , one containing only two and the other only a single carbon atom, have been prepared and combined with various active bases, but without any resolution into optical isomerides being obtained. If isomerism in such a case is possible, the separation of the isomerides is evidently a very difficult one.<sup>26</sup>

The suggestion of van't Hoff, that enantiomorphous forms may exist of compounds containing no asymmetric atom, but deriving their asymmetry from the general structure of the molecule, as in allene derivatives,



and that such isomerides should exhibit optical activity, is one of great theoretical interest, which has not yet been put to an experimental test. An attempt to prepare allene derivatives of the above type, capable of combining with active acids or bases, having proved unsuccessful, compounds have been selected in which symmetrical closed rings replace the double linkings, of which 1-methylcyclohexylidene-4-acetic acid,



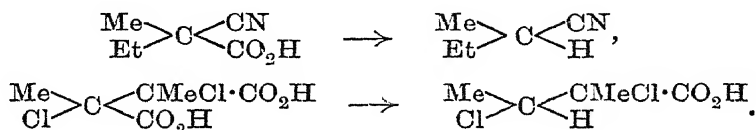
is a typical example. The synthesis of this acid<sup>27</sup> has proved to be a difficult problem, and the product obtained is impure; the test of resolution has therefore not yet been applied. The problem is of such importance for stereochemical theory that it seems advisable to mention the investigation in this place, in spite of its incomplete state.

The problem of a complete asymmetric synthesis, that is, the artificial production of an optically active substance without the intervention of an optically active reagent, has been frequently attacked from

<sup>26</sup> W. J. Pope and J. Read, *Trans*, 1908, 93, 794.

<sup>27</sup> W. H. Perkin, jun., and W. J. Pope, *ibid.*, 1075.

the physical as well as from the chemical side. The use of circularly polarised light has often been suggested and employed for this purpose, so far with entirely negative results. In the latest attempt in this direction<sup>28</sup> the authors point out some of the conditions which must be fulfilled in order that such an attempt may have a prospect of success. The reaction by which the substance is produced must be one which is brought about by light. A reaction which proceeds independently of illumination is not likely to be affected by polarisation of the light falling on the reacting substance. A suitable reaction was found in the removal of carbon dioxide from substituted succinic, malonic, and cyanoacetic acids by light in the presence of uranium salts, as, for instance :



No optical activity of the resulting product was, however, observed when the light was polarised before entering the solution, and the attempt is therefore so far unsuccessful.

A remarkable series of observations is recorded with reference to the separation of active components from a *dl*-mixture.<sup>29</sup> A supersaturated solution containing, for instance, *dl*-sodium ammonium tartrate may be caused to crystallise by the addition of a crystal of the active modification of a tartrate isomorphous or isodimorphous with the dissolved salt, and the crystals separating will have the same sign as the crystal used for inoculation. This is not surprising when the similarity in crystalline structure is taken into account. It is further stated, however, that it is not necessary that the crystal used for inoculation should be optically active. The experiments were principally made with glycine, and when added to a supersaturated solution of *dl*-asparagine, deposition of active asparagine was brought about. It was impossible to predict whether the *d*- or the *l*-form would separate, but the same crystal of glycine always brought about crystallisation of the same isomeride. It is suggested that glycine crystals are hemihedral. If these experiments should be confirmed, and are not found to be due to the presence of optically active substances in the glycine employed, a great advance will have been made in the artificial production of active compounds by an asymmetric synthesis.

Another line of attack which has been adopted by several workers,

<sup>28</sup> F. Henle and H. Haakh, *Ber.*, 1908, **41**, 4261; *A.*, 1909, **i**, 6.

<sup>29</sup> I. Ostromisslensky, *ibid.*, 3035; *A.*, **ii**, 913.

is that of preparing an asymmetric compound in an active solvent, the molecules of which might reasonably be expected to exert a directing influence on the course of the reaction. An attempt of this kind has now been made in the nitrogen series, but without success. Benzylmethylaniline was combined with allyl iodide in a number of optically active solvents, such as *d*-limonene, *l*-menthol, and *l*-menthyl chloromethyl ether, but in no case was an active ammonium iodide obtained.<sup>30</sup>

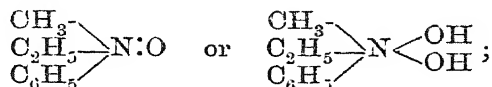
In the continued series of investigations of the influence of solvents on the optical activity of ethyl tartrate, Patterson and his co-workers have examined a large number of halogen and nitro-compounds.<sup>31</sup> Amongst the halogenated solvents, such as alkyl iodides, chloroform, acetylene tetrabromide, etc., many exceptions were again found to the rule that specific rotation varies inversely with solution volume. With aromatic halogen derivatives, well-marked minima of rotation were observed at certain concentrations. The changes of rotation with temperature were also examined, and solutions in  $\alpha$ -bromonaphthalene were found to have a maximum rotation at 94°, the case resembling that of dilute solutions of alkyl tartrates in water, the rotation-temperature curve of which also passes through a maximum. A wider range of activity was observed when aromatic nitro-compounds were used as solvents, the specific rotation at infinite dilution in  $\alpha$ -nitronaphthalene being about +65°, and in *s*-trinitrobenzene about -30°. The relation between the maximum rotation and the temperature at which it occurs is fairly independent of the nature of the solvent and of the concentration. As in the problem of the relation of activity to asymmetry, it is evident that in spite of the vast quantity of experimental material that has been accumulated, the complete theoretical explanation is far from having been attained.

Two forms of asymmetry have been observed in nitrogen compounds, the first, in substances containing tervalent nitrogen doubly linked with carbon or nitrogen, as in oximes and diazo-compounds; the second, in substances containing quinquivalent nitrogen. So far, activity has only been observed in the latter class when the five substituting groups are all different, although four different groups should suffice to produce asymmetry. A new class of active substances has now been found, in which two valencies of the nitrogen atom are united to the same, or similar, atoms. Methylethylaniline oxide, for example, has been resolved into two active components by conversion into the

<sup>30</sup> E. Wedekind and O. Wedekind, *Ber.*, 1908, **41**, 456; *A.*, i, 258.

<sup>31</sup> T. S. Patterson and D. Thomson, *Trans.*, 1908, **93**, 355; T. S. Patterson and D. P. McDonald, *ibid.*, 936; T. S. Patterson, *ibid.*, 1836.

*d*-camphorsulphonate. The solution of the active oxide, which is a very weak base, must contain



in either case, the number of different groups united with the nitrogen atom is only four. If the compound present in the solution of the base has the second formula, the positions of the two hydroxyls cannot be identical, since the addition of hydrochloric acid produces a salt having the same activity as the base. It is concluded that four of the valencies of a quinquivalent nitrogen atom are directed, like those of a carbon atom, to the angles of a tetrahedron, the fifth (ionisable) valency being mobile. Isomerism would then occur whenever the groups attached by the four fixed valencies were different.<sup>32</sup>

Active piperidine derivatives having a large substituent in position 2, and an alkyl attached to the nitrogen atom, have been found to yield two stereoisomeric quaternary salts with alkyl haloids, only a single product being obtained when the substituting group in position 2 is absent or small. This has been further confirmed by the examination of  $\alpha$ - and  $\beta$ -pipercoline derivatives, benzyl haloids being added to the *l*-bases. In neither case were optical isomerides obtained.<sup>33</sup>

Turning now from the production of active substances to their resolution and racemisation, the preparation of the two active forms of benzoin has now been accomplished. *l*-Mandelic acid is converted into the amide, and this is combined with magnesium phenyl bromide, yielding *l*-benzoin. The *d*-isomeride is prepared in a similar way. With the exception of *l*ævulose, no keto-alcohol had previously been resolved into its optically active components.<sup>34</sup>

The autoracemisation of active ammonium salts in solution has been the subject of controversy,<sup>35</sup> but it now appears certain from cryoscopic measurements and from comparative determinations of the velocity of dissociation and of change in rotation, that the observed alteration in rotation is due to the breaking up of the ammonium salt in solution into tertiary amine and alkyl halide.

A case of partial racemisation has been observed in the hydrogen tartrate of hydroquinaldine.<sup>36</sup>

The Walden inversion has been the subject of several investigations.

<sup>32</sup> J. Meisenheimer, *Ber.*, 1908, **41**, 3966; *A.*, 1909, i, 20.

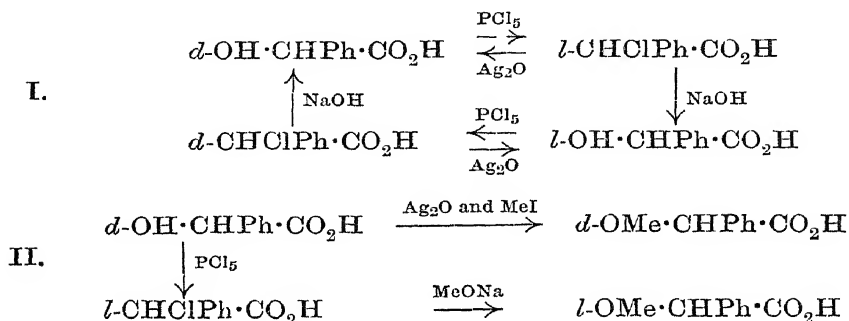
<sup>33</sup> M. Scholtz, *ibid.*, 2005; *A.*, i, 678.

<sup>34</sup> A. McKenzie and H. Wren, *Trans.*, 1908, **93**, 309.

<sup>35</sup> E. Wedekind, O. Wedekind, and F. Paschke, *Ber.*, 1908, **41**, 1029, 2659; *A.*, i, 334, 722; H. von Halban, *ibid.*, 2417; *A.*, i, 627.

<sup>36</sup> A. Ladenburg and W. Hermann, *ibid.*, 966; *A.*, i, 364.

The replacement of halogen by hydroxyl or methoxyl in phenylchloroacetic acid has been examined from this point of view, the results being expressed in the two following schemes :



It appears from this that in the interconversion of the mandelic acids, sodium hydroxide behaves abnormally and silver oxide normally.<sup>37</sup>

E. Fischer has also continued his investigations on the same subject,<sup>38</sup> and finds that valine ( $\alpha$ -aminoisovaleric acid) remains optically unchanged after conversion into the bromo-fatty acid and back again into the amino-compound. It is suspected, however, that this result is due rather to a double Walden inversion than to its absence. This exceptional behaviour is attributed to the influence of the *isopropyl* group. Active aminophenylacetic acid is racemised so rapidly by nitrosyl bromide or nitrous acid that pure active products could not be obtained.

It is only possible to refer to a few more papers dealing with stereo-isomerism. A method of determining the configuration of  $\alpha$ -dioximes is furnished by the fact that of the possible isomerides, only the *syn*-modification has the property of forming complex metallic dioximines.<sup>39</sup> The method has been tested in a number of cases, and has been applied to several  $\alpha$ -dioximes of previously unknown configuration.

No marked difference is to be found between the dielectric constants of *d*-, *l*-, and *i*-modifications of asymmetric compounds. Ethyl racemate, however, has a much greater absorptive power for electric waves than the tartrate, and, since hydroxylic groups are the principal cause of such absorption, this suggests that the hydroxyls are mainly concerned in the formation of the racemic compound.<sup>40</sup>

The viscosity of a solution of a racemic salt is always less than that

<sup>37</sup> A. McKenzie and G. W. Clough, *Trans.*, 1908, **93**, 811.

<sup>38</sup> E. Fischer and H. Scheibler, *Ber.*, 1908, **41**, 889, 2891; *A.*, i, 324, 857; E. Fischer and O. Weichhold, *ibid.*, 1286; *A.*, i, 419.

<sup>39</sup> L. Tschugaëff, *ibid.*, 1678; *A.*, i, 554.

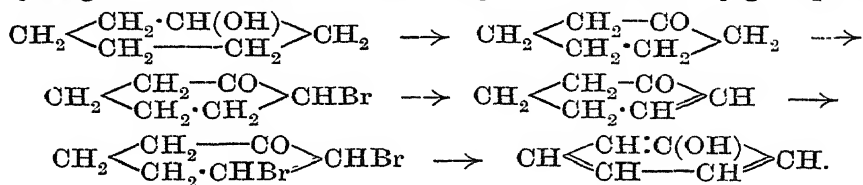
<sup>40</sup> A. W. Stewart, *Trans.*, 1908, **93**, 1059.

of the active components, but the difference is very small. The transition point of the racemate also appears as a break in the temperature-viscosity curve.<sup>41</sup>

*Some Reactions of the Cyclic Hydrocarbons and their Derivatives.*

1. *Aromatic from Hydroaromatic Compounds.*—The conversion of aromatic substances into hydroaromatic derivatives by hydrogen and a catalyst has already been mentioned. An interesting case of the converse change has recently been worked out, in which phenol has been produced from *cyclohexanol* in such a way that the intermediate products could be isolated, showing the gradual transition from the saturated to the aromatic ring.

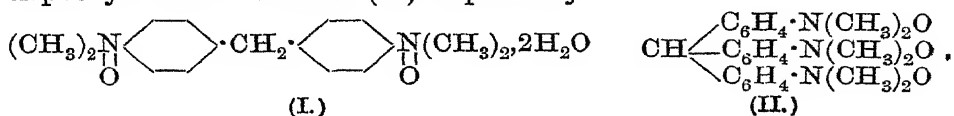
*cyclo*Hexanone, obtained by the oxidising action of bromine or chlorine from the saturated alcohol, was brominated to 1-bromocyclohexanone. The elimination of hydrogen bromide led to  $\Delta^2$ -cyclohexenone; addition of bromine to this substance, followed by removal of hydrogen bromide from the resulting dibromide, finally gave phenol:



Ethyl *cyclohexane*-2-carboxylate is converted into salicylic acid by a precisely similar series of changes.<sup>42</sup>

2. *Oxidation of Aromatic Substances.*—Although the aromatic hydrocarbons (benzene, naphthalene, etc.) are not themselves oxidised to definite products by chromyl chloride yet, the corresponding aldehydes are readily obtained with this oxidising agent from the *m*- and *p*-nitrotoluenes and the three isomeric chlorotoluenes. In a similar manner, diphenylmethane and triphenylmethane are converted quantitatively into benzophenone and triphenylcarbinol respectively.<sup>43</sup>

Caro's acid has been successfully applied to the preparation of tertiary amine oxides; tetramethyldiaminodiphenylmethane and hexamethyltriaminotriphenylmethane having been thus converted into tetramethyldiaminodiphenylmethane dioxide (I) and hexamethyltriaminotriphenylmethane trioxide (II) respectively.



<sup>41</sup> A. E. Dunstan and F. B. Thole, *Trans.*, 1908, **93**, 1815.

<sup>42</sup> A. Kotz and C. Gotz, *Annalen*, 1907, **358**, 183; *A.*, i, 173.

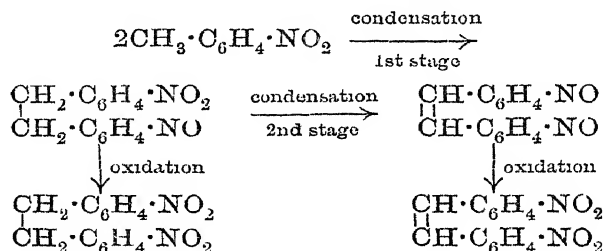
<sup>43</sup> H. D. Law and F. M. Perkin, *Trans.*, 1908, **93**, 1633.

The reactions of these amine oxides are of interest ; sulphur dioxide and nitrous acid convert them respectively into the sulphonic acids and nitro-derivatives of the original tertiary bases. In these reactions the



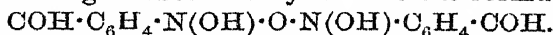
oxygen atoms of the di- and tri-oxides become involved, and the substituents take up ortho-positions with respect to the nitrogen atoms.<sup>44</sup> The oxidation of acetyl-*p*-phenylenediamine by Caro's acid results in the formation of *p*-nitrosoacetanilide (green plates, m. p. 175°), which is transformed by water into its colourless, bimolecular polymeride (m. p. 181°).<sup>45</sup>

The technically important conversion of *p*-nitrotoluene and its derivatives into stilbene compounds has been further investigated, the results showing that the following scheme of condensation in two stages, accompanied at each stage by aerial oxidation, furnishes an explanation which is generally true of these condensations.

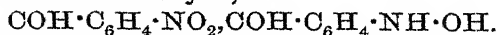


4-Nitro-*o*-xylene and 4-nitro-2-methoxy<sup>+</sup>luene with methyl-alcoholic potash and aerial oxidation gave chiefly 4:4'-dinitro-2:2'-dimethylstilbene and 4:4'-dinitro-2:2'-methoxystilbene. Similar changes occurred with 4-nitro-*o*-toluic acid and 2:4-dinitrotoluene, but in the former case sodium hypochlorite, and in the latter, iodine were employed as oxidising agents.<sup>46</sup>

3. *Reduction of Aromatic Nitro-compounds*.—A new phase in the reduction of nitro-groups has been observed by G. Heller and A. Sourlis,<sup>47</sup> who also correct an earlier statement of Bamberger's,<sup>48</sup> that his so-called "agnetobenzaldehyde" has the formula



This substance is really a molecular compound of *o*-nitrobenzaldehyde and *o*-hydroxylaminobenzaldehyde,



They find, however, that the reduction of *o*-nitromandelonitrile with

<sup>44</sup> E. Bamberger and L. Rudolf, *Ber.*, 1908, 41, 3290 ; *A.*, i, 1011.

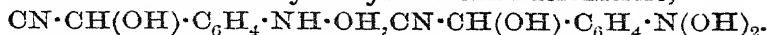
<sup>45</sup> J. O. Cain, *Trans.*, 1908, 93, 686.

<sup>46</sup> A. G. Green and J. Baddiley, *ibid.*, 1721.

<sup>47</sup> *Ber.*, 1908, 41, 373 ; *A.*, i, 208.

<sup>48</sup> *Ibid.*, 1906, 39, 4252 ; *A.*, 1907, i, 163.

zinc dust leads to the formation of a molecular compound of hydroxylaminomandelonitrile and dihydroxylaminomandelonitrile,



This product on treatment with phenylhydrazine yields hydroxyisatinphenylhydrazine and the  $\alpha$ - and  $\beta$ -phenylhydrazones of isatin.

The reduction of nitro-compounds by alcoholic ammonium sulphide, which was first practised by Zinin in 1842, has been further developed in recent years. In 1902 and subsequently, J. B. Cohen and others showed that hydroxylamino-derivatives were produced by the partial reduction of trinitrobenzene and trinitrotoluene with hydrogen sulphide in the presence of a small amount of ammonia. They also found that chloronitro-compounds and alkyl dinitrobenzoates likewise gave hydroxylamines under similar conditions.<sup>49</sup> The fact that this change,  $\text{R}\cdot\text{NO}_2 \rightarrow \text{R}\cdot\text{NH}\cdot\text{OH}$ , occurs generally, has been further demonstrated by reducing the simpler nitro-compounds with alcoholic ammonium sulphide in the cold, when excellent yields of the corresponding arylhydroxylamines were obtained. For example,  $\alpha$ -nitronaphthalene gives  $\alpha$ -naphthylhydroxylamine, from which  $\alpha$ -nitrosonaphthalene is easily produced by oxidation with silver oxide or lead peroxide in anhydrous solvents.<sup>50</sup>

It has generally been assumed that the azoxy-compounds formed during reduction by a condensation of the nitroso- and hydroxylamino-derivatives can only arise in neutral or alkaline solutions. But in certain cases this condensation may occur even in the presence of mineral acids. The reduction of certain substituted nitro- and dinitro-compounds has been systematically examined, the results showing that (1) condensation and reduction of the intermediate nitroso- and hydroxylamino-derivatives both proceed at a measurable rate whether the solution be acid, neutral, or alkaline; (2) condensation is induced by the presence of tervalent nitrogen in the free arylhydroxylamine, the quinquevalent nitrogen of the hydroxylamine salt being incapable of condensation.<sup>51</sup>

4. *Formation of Aromatic Hydroxylic Compounds.*—In practice the introduction of hydroxyl into the nucleus of an aromatic hydrocarbon requires several operations, although small amounts of nitrated phenols are produced during many nitrations. According to a recent patent, a mixture of benzene, strong nitric acid, and mercuric nitrate gives a fairly good yield of picric acid, together with smaller amounts of nitrobenzene and *o*-nitrophenol.<sup>52</sup>

The nitration process may be divided into two phases, in the second

<sup>49</sup> *Trans.*, 1902, **81**, 26; 1905, **87**, 1257.

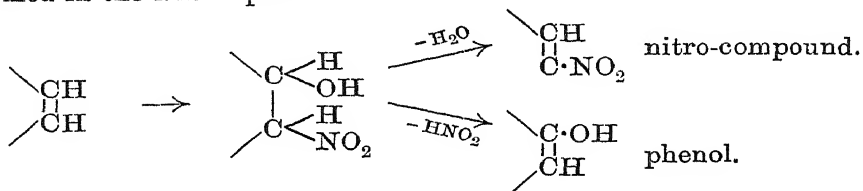
<sup>50</sup> R. Willstätter and H. Kubli, *Ber.*, 1908, **41**, 1936; *A.* i, 522.

<sup>51</sup> B. Flurschein and T. Simon, *Trans.*, 1908, **93**, 1463.

<sup>52</sup> R. Wolfenstein and O. Boters, D.R.-P. 194883; *A.*, i, 629.



of which water is usually eliminated from the additive compound formed in the initial phase :



The alternative elimination of nitrous acid leads to the production of phenolic compounds.

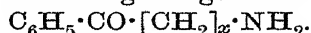
The direct introduction of hydroxyl groups into the anthracene molecule has been effected, and alizarin, free from by-products, may be produced by heating anthraquinone with potassium chlorate and aqueous alkali hydroxide at 200°. <sup>53</sup>

Similarly, anthrarufin (1:5-dihydroxyanthraquinone) and chrysazin (1:8-dihydroxyanthraquinone) yield respectively the 1:2:5- and 1:2:8-trihydroxyanthraquinones when they are heated at 180—185° with sodium nitrate and aqueous alkalis, a mixture of potassium and sodium hydroxides giving the best result. <sup>54</sup>

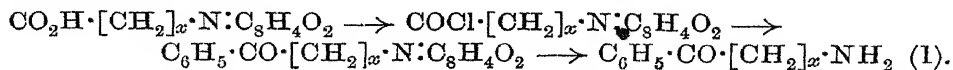
### Ring Formation.

The general tendency which undoubtedly exists for the formation of five- or six-membered rings in preference to those containing fewer or more components, is usually explained in terms of von Baeyer's strain hypothesis, to which reference was made in last year's Report (p. 138). The new cases of ring formation observed during the past year furnish further confirmation of the validity of this generalisation.

A striking illustration of the way in which the above tendency affects the properties of straight-chain compounds is afforded by a study of the aminoketones having the general formula



A general method has been devised for preparing these substances, which consists in converting the phthalimino-aliphatic acids into their chlorides, and then condensing these with benzene in the presence of aluminium chloride : <sup>55</sup>



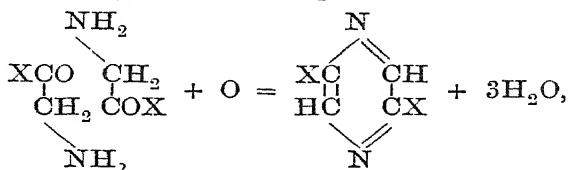
Acid hydrolysis of the ketone leads to fission at the double linking,

<sup>53</sup> D.R.-P. 116526 ; *A.*, i, 191.

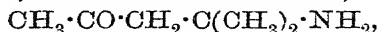
<sup>54</sup> D.R.-P. 196980 and 195028 ; *A.*, i, 807.

<sup>55</sup> S. Gabriel, *Ber.*, 1907, **40**, 2649 ; 1908, **41**, 1127 ; *A.*, 1907, i, 625 ; 1908, i, 464.

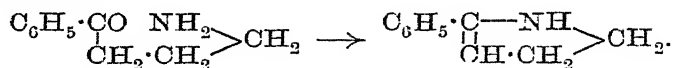
when phthalic acid and the salt of the aminoketone (I) are set free. It was at once seen that the stability of these compounds varied considerably with the value of  $\alpha$ . The  $\alpha$ -aminoketones corresponding with  $\alpha = 1$  are only known in the form of their salts. When liberated therefrom, they undergo simultaneously condensation and oxidation, so that a six-membered pyrazine ring is produced.



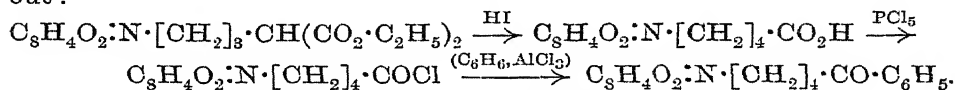
The  $\beta$ -aminoketones, such as diacetoneamine,



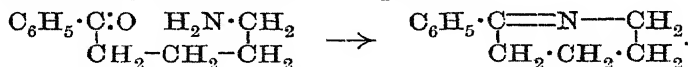
are stable, and can be isolated without showing any tendency to undergo cyclic condensation into four- or eight-membered rings. The  $\gamma$ -aminoketones are so unstable that even in the form of their hydrochlorides, condensation occurs with the production of a five-membered ring; thus phenyl  $\gamma$ -aminopropyl ketone gives rise to 2-phenylpyrroline:



The  $\delta$ -aminoketones are as unstable as the  $\gamma$ -compounds. In preparing one of these, the following series of operations was carried out:



Hydrolysis of the final product,  $\delta$ -phthaliminovalerophenone, gave rise, not to  $\delta$ -aminovalerophenone, but to 2-phenyltetrahydropyridine, the six-membered cyclic condensation product:

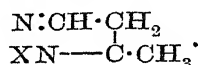


The  $\epsilon$ -aminoketones, for example,  $\epsilon$ -aminocaprophenone, which might give rise to seven-membered rings, are quite stable under conditions in which the  $\gamma$ - and  $\delta$ -aminoketones condense to pyrrole and pyridine derivatives respectively.<sup>56</sup>

The stability of  $\beta$ -substituted ketones disappears in the presence of a reagent capable of condensing so as to form a five-membered ring. Methyl  $\beta$ -chloroethyl ketone condenses in this way with hydroxylamine, phenylhydrazine, or any of the reagents used in detecting carbonyl oxygen.

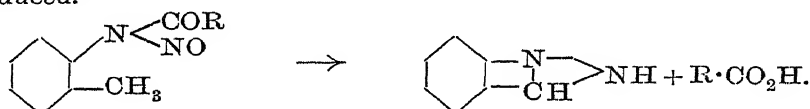
<sup>56</sup> S. Gabriel and J. Colman, *Ber.*, 1908, **41**, 2010, 2014; *A.*, i, 648, 649.

An isooxazoline,  $\text{N} \begin{smallmatrix} \text{CH} \cdot \text{CH}_2 \\ \text{O} - \text{C} \cdot \text{CH}_3 \end{smallmatrix}$ , is produced with hydroxylamine, whilst hydrazine and phenylhydrazine yield pyrazolines,<sup>57</sup>

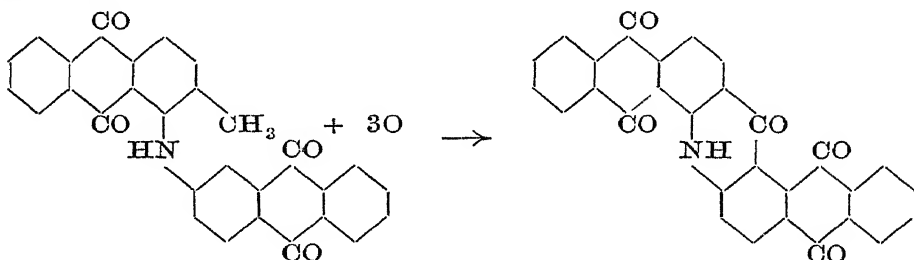


A methyl group situated in an aromatic nucleus generally preserves its inert paraffinoid character, but the tendency for ring formation may become sufficiently great to overcome this inertia, and the methane carbon atom then becomes involved in the formation of a new ring.

When the nitrosoacetyl-*o*-toluidines are gently warmed in an anhydrous solvent, a condensation of this kind occurs and an indazole is produced.<sup>58</sup>

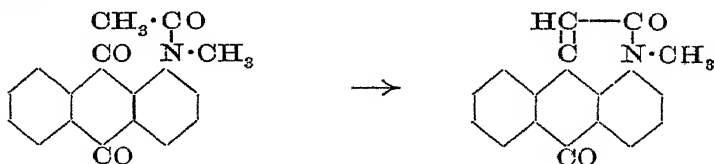


The intervention of a methyl substituent also occurs when a mixture of 2-methyl-1 : 2'-dianthraquinonylamine and lead oxide are added to aqueous potassium hydroxide at 170°.



*as*-Dianthraquinonyl-*p*-acridone thus produced is a red substance, which on reduction gives an oxidisable, violet leuco-derivative.<sup>59</sup>

Several ortho-acridones of the anthracene series have been obtained by the condensation of acetylmethyl-1-aminoanthraquinone and its derivatives.



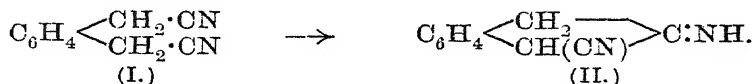
<sup>57</sup> M. Maire, *Bull. Soc. chim.*, 1908, [iv], **3**, 272; *A.*, i, 290.

<sup>58</sup> P. Jacobson and L. Huber, *Ber.*, 1908, **41**, 660; *A.*, i, 298.

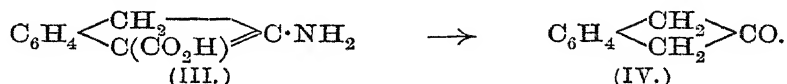
<sup>59</sup> D.R.-P. 192436; *A.*, i, 456.

In these substances the methyl radicle is in an aliphatic group, but, nevertheless, the same tendency to the formation of six-membered rings underlies the condensation.<sup>60</sup>

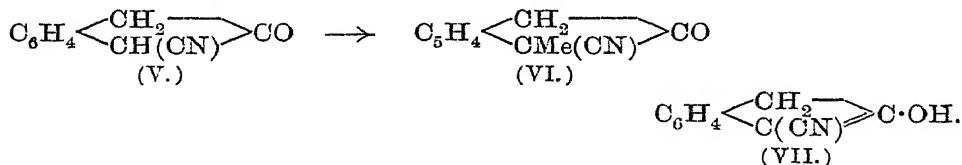
*o*-Phenylenediacetonitrile (I), when warmed in alcoholic solution containing a trace of sodium ethoxide, undergoes molecular rearrangement into  $\beta$ -imino- $\alpha$ -cyanohydrindene (II):



This product gives all the reactions of an imino-derivative, but when the cyanogen group is replaced by  $\text{CO}_2\text{H}$ ,  $\text{CO}_2 \cdot \text{C}_2\text{H}_5$ , or  $\text{CO} \cdot \text{NH}_2$ , then the structure changes to that of an aminoindene. The acid (III) does not lose its nitrogen until after carbon dioxide has been eliminated, when  $\beta$ -hydrindone (IV) is produced:

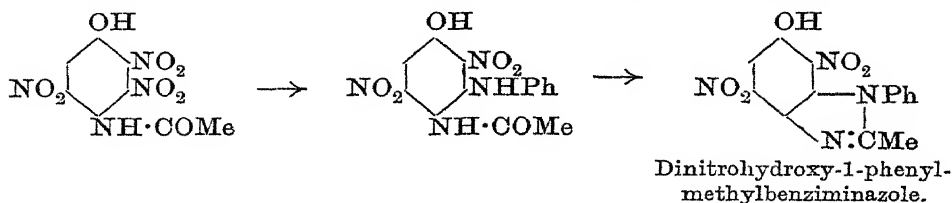


The above  $\beta$ -imino- $\alpha$ -cyanohydrindene is hydrolysed by dilute acids into  $\alpha$ -cyano- $\beta$ -hydrindone (V); this compound yields a phenylhydrazone and a *C*-methyl derivative (VI), but also reacts in its enolic form (VII) to give rise to acyl and *o*-alkyl derivatives:



These results afford an interesting example of the formation of a five-membered ring, the structure of which is greatly influenced by the nature of its substituents.<sup>61</sup>

The interaction of the primary aromatic amines and 2 : 3 : 5-trinitro-4-acetylaminophenol, a substance containing a singularly mobile nitro-group in position 3, leads to the production of iminazoles:

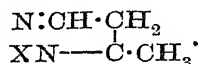


In some cases the intermediate product can be isolated, but

<sup>60</sup> D.R.-P. 192201; *A.*, i, 456.

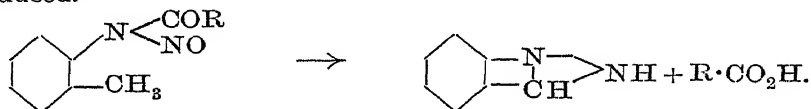
<sup>61</sup> C. W. Moore and J. F. Thorpe, *Trans.*, 1908, **93**, 165.

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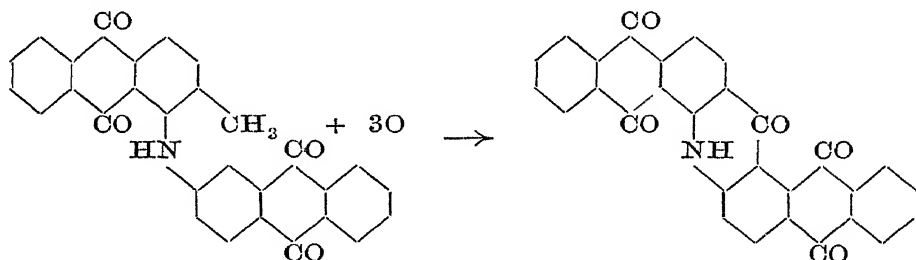


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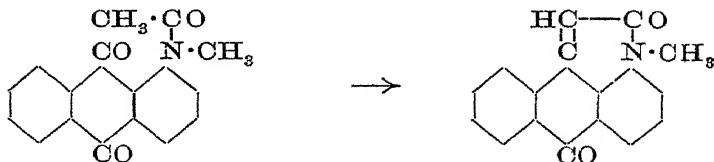


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<sup>57</sup> M. Maire, *Bull. Soc. chim.*, 1908, [iv], **3**, 272; *A.*, i, 290.

<sup>58</sup> P. Jacobson and L. Huber, *Ber.*, 1908, **41**, 660; *A.*, i, 298.

<sup>59</sup> D.R.-P. 192436; *A.*, i, 456.

worked out for the synthesis of tetrahydrocarbazole and its homologues :

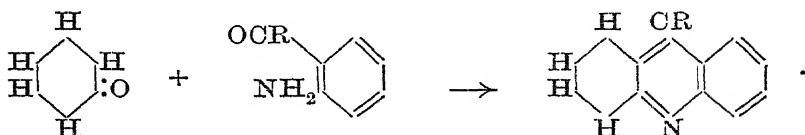


Tetrahydrocarbazole.

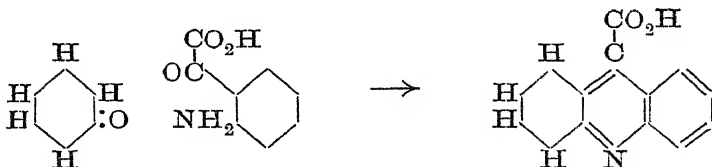
The aromatic hydrazones of these cyclic ketones undergo condensation when gently warmed with dilute acids. The reaction is general for all aromatic hydrazines containing one free ortho-position, but only takes place with simple saturated cyclic ketones, and not with those containing either unsaturated or bridged rings.<sup>66</sup>

Tetrahydrogenated acridines have been obtained from the cyclic ketones by the following methods.

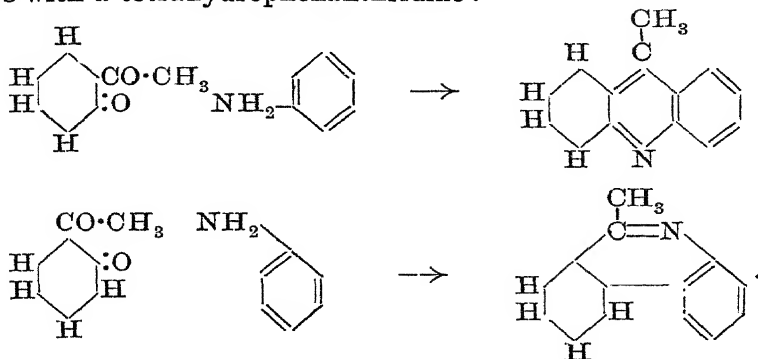
1. Condensation with aromatic *o*-amino-aldehydes and ketones :



2. Condensation with isatin and alkali hydroxides :



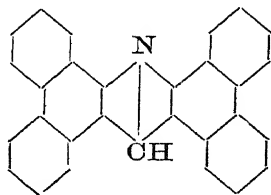
3. Condensation of the *o*-acylketohexamethylenes with aniline and its homologues. This process leads to a mixture of a tetrahydro-acridine with a tetrahydrophenanthridine :



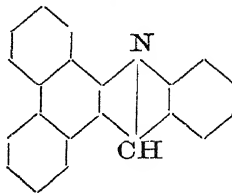
<sup>66</sup> W. Borsche, *Annalen*, 1908, 359, 49; *A.*, i, 365.

The foregoing hydroaromatic carbazoles and acridines can be transformed into the corresponding aromatic compounds by heating with lead oxide.<sup>67</sup>

Diphenanthracridine (I) and phenophenanthracridine (II) have



(I.)



(II.)

been prepared, the first by condensing 9-aminophenanthrene with methylene halides, and the second, by treating the same base with *o*-nitrobenzyl chloride and stannous chloride.<sup>68</sup>

The foregoing cases of ring formation are all examples of the general tendency to the production of five- and six-membered cyclic systems. This rule is not, however, without important exceptions, and seven- and eight-membered rings do occasionally make their appearance. The *cyclooctadienes*, mentioned in connexion with the chemistry of the terpenes and indiarubber, contain a ring of eight carbon atoms.

The following remarkable series of reactions, published towards the close of 1907, illustrate the exceptional case of the conversion of a benzene nucleus into a seven-membered ring.

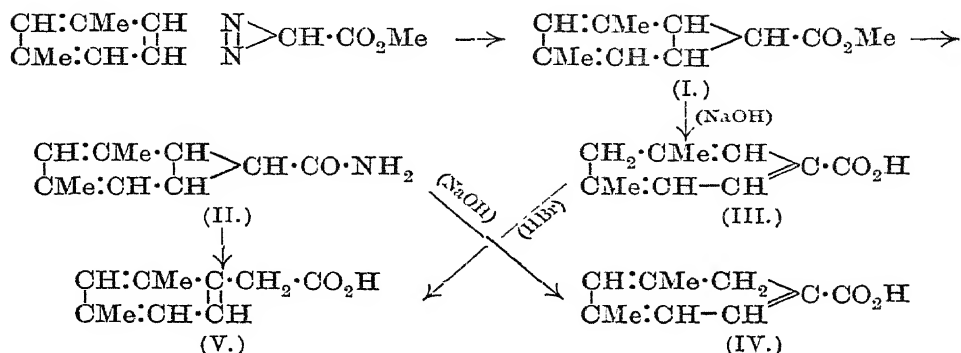
Reference has already been made, under the heading of aliphatic diazo-compounds, to the great variety of products obtainable from ethyl diazoacetate. One of the most remarkable properties of this ester is its reaction with benzene and its homologues. When gently warmed with one of these hydrocarbons, nitrogen is evolved, and the bivalent residue,  $\text{CO}_2\text{Et}\cdot\text{CH}<$ , attaches itself to two contiguous carbon atoms of the aromatic nucleus with the formation of a bicyclic system, consisting, as a whole, of a seven-membered ring, but divided internally by a bridged linking into two cyclic components, one containing three, and the other six, members. The case of *m*-xylene was described in the last communication on this subject, and as it resembles those of toluene and benzene, it may be taken as an illustration of this condensation.

Inasmuch as the bicyclic structure is like that existing in carone, the initial product receives a name derived by transposition from that of the analogously constituted ketone. This methyl 1:3-dimethylnorcardienecarboxylate (I), so far, retains an aliphatic character, that

<sup>67</sup> Borsche, *Ber.*, 1908, 41, 2203; *A.*, i, 682.

<sup>68</sup> P. C. Austin, *Trans.*, 1908, 93, 1760.

it yields the amide (II) on treatment with ammonia. Alkaline hydrolysis, however, converts it into a monocyclic acid (III), 3:5-dimethylcyclo- $\Delta^{2,5}$ -heptatriene-1-carboxylic acid. The amide gives rise to the isomeric 3:5-dimethylcyclo- $\Delta^{3,5}$ -heptatriene-1-carboxylic acid (IV) when hydrolysed with alkalis, but under the influence of acids the heptatriene ring is transformed again into a benzene ring, and 3:5-dimethylphenyl-4-acetic acid (V), isomeric with the two heptatrienecarboxylic acids, is produced.<sup>69</sup>



### *Mordant Colours as Heterocyclic Complexes.*

The theory that the colours produced on mordanted fabrics owe their existence to the formation of heterocyclic complexes in which the metallic oxide or hydroxide becomes a component of the ring, has been discussed by A. Werner and C. Liebermann. Both agree on the general principle that the peculiar properties of these lakes are due to a ring structure involving the metallic base. The great stability and sparing solubility of lakes, the remarkable differences between their colours and those of the ordinary salts containing the same metal, and the singular fact that in many cases the metal does not exhibit certain of its characteristic analytical reactions, all justify the theory of a heterocyclic constitution for these dyes.

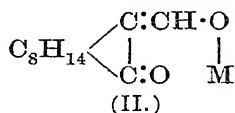
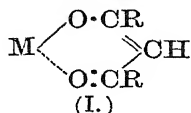
Werner adduces many instances in which ring structure is possible only on the assumption that both the principal and secondary valencies of the metal are involved in ring formation.

Benzoylacetone and similar compounds are shown to behave as weak dyes on mordanted cotton. The lakes thus produced must be similar in structure to the closely allied metallic acetylacetonates, to which on account of their great stability a co-ordinated constitution is ascribed. Accordingly these lakes are also formulated as co-

<sup>69</sup> E. Buchner and K. Delbrück, *Annalen*, 1907, **358**, 1; *A.*, i, 87.

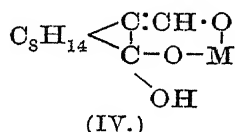
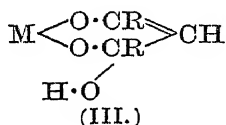


ordinated compounds (I), where R is an alkyl or acyl radicle and M is the metal.

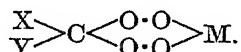


This view of their constitution is justified by the fact that hydroxymethylenecamphor, a compound in which the keto-enolic structure is the stable form, also behaves as a mordant dye, the lakes of which must have the above formula (II).

Liebermann, on the other hand, assumes that in those cases where a carbonyl group is contiguous to the hydroxyl or isonitroso-radicle, it is only necessary to make the very reasonable assumption that this group reacts in its hydrated form (III and IV), and then the older theory becomes sufficiently comprehensive to include all cases of mordant dyeing without recourse to the hypothesis of supplementary valency.



Werner, in reply, points to the fact that the ordinary theory of valency does not account for the great difference in colour and stability between the lakes and the colourless salts of certain dibasic acids, many of which also possess a cyclic structure:



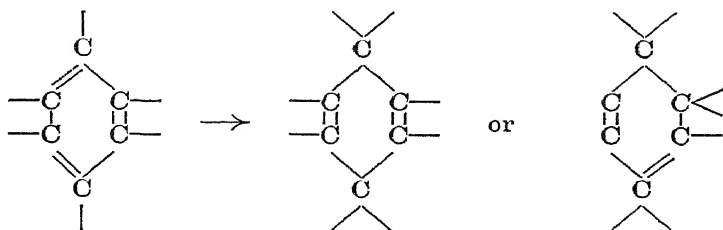
According to Werner the production of a metallic heterocyclic complex leads to the development of colour and other properties peculiar to lakes only when both the supplementary and principal valencies of the metal are involved in the structure of the ring.<sup>70</sup>

### Quinones.

The interest attaching to the aromatic diketones and their derivatives is due to the fact that the existence of these compounds affords justification for the assumption so frequently made that the first phase in the interactions of aromatic substances and various reagents is the formation of an additive product in which the valencies of the aromatic nucleus have undergone a certain rearrangement. When the new arrangement persists in the final product, this substance is regarded as a quinone derivative or quinoid.

<sup>70</sup> A. Werner, *Ber.*, 1908, **41**, 1062, 2383; *A.*, i, 440; C. Liebermann, *ibid.*, 1436; *A.*, i, 441.

In the simplest case of benzene, we may have the change from  $C_6H_4^{II}$  to  $p$ - or  $o$ - $C_6H_4^{IV}$



Corresponding with these two types of rearrangement there exist the long known  $p$ -benzoquinone and the more recently discovered  $o$ -benzoquinone.

At first only quinones of the ortho- and para-series were known, but lately the possibilities of quinonoid rearrangement have been considerably extended by Willstätter and his collaborators. In 1907 it was shown that 2 : 6-dihydroxynaphthalene could be oxidised so as to yield the corresponding 2 : 6-naphthaquinone,<sup>71</sup>



whilst 1 : 5-dichloro-2 : 6-dihydroxynaphthalene furnishes 1 : 5-dichloro-2 : 6-naphthaquinone, a substance possessed of considerable stability.

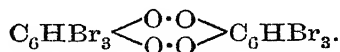
In continuing the study of  $o$ -benzoquinone it has been found that when catechol is rapidly oxidised (15 seconds) with pure silver oxide in dry ether a colourless modification of the quinone can be isolated. This colourless variety, which is very unstable and changes quickly into the red modification, is also obtained when an ethereal solution of the latter is cooled. The two forms are therefore in equilibrium in solution. These isomerides are represented by the following formulæ, the colourless variety being regarded, not as a quinone, but as a benzene peroxide.<sup>72</sup>



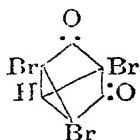
<sup>71</sup> R. Willstätter and J. Parnas, *Ber.*, 1907, **40**, 3971 ; *A.*, 1907, i, 1056.

<sup>72</sup> R. Willstätter and F. Müller, *ibid.*, 1908, **41**, 2580 ; *A.*, i, 731.

The colour of *m*-nitroaniline and its derivatives was long ago ascribed by H. E. Armstrong to the existence of a dynamic form having a meta-quinonoid structure, and more recently Baly has referred to the possibility of a meta-quinonoid rearrangement. These speculations have now been justified by the revision of the constitution of tribromoresoquinone, a yellowish-red substance originally discovered in 1872 by Liebermann and Dittler, who prepared it by removing two bromine atoms from tribromoresorcinol dibromide, and gave it the formula



Molecular-weight determinations in boiling benzene have now shown that the substance has the simpler formula  $\text{C}_6\text{HO}_2\text{Br}_3$ , and as it liberates iodine from potassium iodide, it is regarded as a meta-quinone, namely, 2 : 4 : 6-tribromo-*m*-benzoquinone,<sup>73</sup>



This substance gives neither oxime nor hydrazone, for hydroxylamine and phenylhydrazine behave towards it as reducing agents and convert it into tetrabromodiresorcinol,  $\text{C}_6\text{HBr}_2(\text{OH})_3 \cdot \text{C}_6\text{HBr}_2(\text{OH})_2$ .

One of the most characteristic reactions of quinones is the formation of intensely coloured additive compounds with their reduction products; quinhydrone produced by the combination of *p*-benzoquinone and quinol in molecular proportions being perhaps the best known example of this class of substances. That this property is not restricted to para-quinones is shown by the fact that tetrachloro-*o*-benzoquinone combines with tetrachlorocatechol to form octachloro-*o*-quinhydrone,  $\text{C}_6\text{Cl}_4\text{O}_2 \cdot \text{C}_6\text{H}_2\text{Cl}_4\text{O}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ , a substance separating in lustrous, black needles.<sup>74</sup> Willstätter proposes to call these additive compounds, which consist only partly of a quinonoid complex, *meriquinoids*, whilst the quinones themselves and their derivatives (imines, etc.) are termed *holoquinoids*. The formation of the meriquinoids is attributed to the residual affinity of the quinonoid oxygen atoms, or in the case of the quinoneimines to that of the imino-group. The intense colour of the additive product is considered to be due to an oscillation (isorropesis) of the quinone linking between the two

<sup>73</sup> R. Meyer and K. Desamari, *Ber.*, 1908, 41, 2437; *A.*, i, 658.

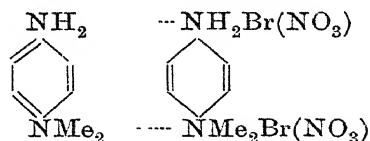
<sup>74</sup> C. L. Jackson and P. W. Carleton, *Amer. Chem. J.*, 1908, 39, 493; *A.*, i, 427.

components of the molecular compound. In this way the colour of the meriquinoids is referred to the same cause as that which is assumed by von Baeyer to be operative in the di- and tri-phenylmethane colouring matters, namely, the oscillation of the quinonoid condition between two or three aromatic nuclei.

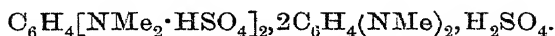
These views on the colour of quinhydrones and meriquinoids are not accepted unreservedly by F. Kehrman,<sup>75</sup> who objects to the parallel drawn between quinoneimines and their meriquinoid salts, on the one hand, and the triphenylmethane-imine bases and their salts on the other. In the first case, the intensification of colour is due to the introduction of auxochromic groups ( $\text{NH}_2$  or  $\text{OH}$ ) without any modification of the chromophore; in the second, the bases and their salts are quite different in constitution, and the variation of colour is due to this complete change in the configuration of the chromophore. The difference in stability between the ordinary quinhydrones and the meriquinoids (Wurster's salts, etc.) is merely one of degree, and there is no reason for assuming that these two types of partial quinoids differ essentially in constitution.

The coloured salts formerly obtained by C. Wurster<sup>76</sup> on oxidising alkylated *p*-diamines are regarded as meriquinoids by Willstätter.

The red salt produced by the action of bromine on *as*-dimethyl-*p*-phenylenediamine is *meriquinonedimethyldi-imonium* bromide,



The nitrate has also been obtained, and the blue salt from tetramethyl-*p*-phenylenediamine contains a sulphate which is only one-third quinonoid,



Benzidine gives rise to two meriquinonoid chromates, whilst both holo- and meri-quinoids have been obtained from tetramethylbenzidine.<sup>77</sup>

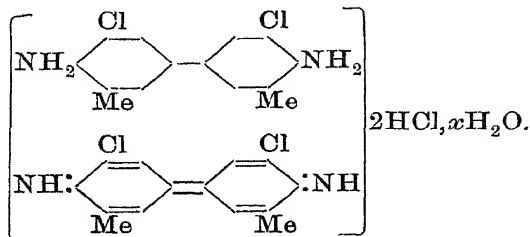
Further investigations on the oxidation products of benzidine, diphenylene, and tolidine have resulted in the production of diphenquinonedichlorodi-imide,  $\text{NCl}:\text{C}_6\text{H}_4:\text{C}_6\text{H}_4:\text{NCl}$ , ditoluquinonedichloro-

<sup>75</sup> *Ber.*, 1908, **41**, 2340; *A.*, i, 698.

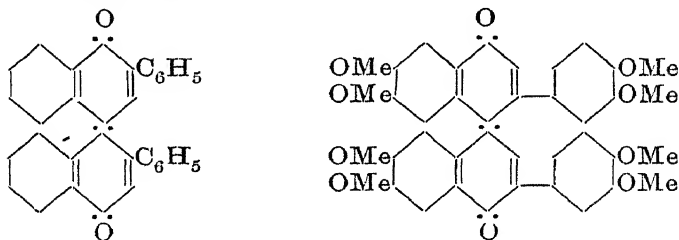
<sup>76</sup> *Ibid.*, 1879, **12**, 1803; 1887, **20**, 2071.

<sup>77</sup> R. Willstätter and J. Piccard, *ibid.*, 1908, **41**, 1458 and 3245; *A.*, i, 475, 915.

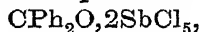
di-imide, *holo*- and *meri*-dichloroditoluquinonedi-imonium chlorides, the last of these having the composition <sup>78</sup>



The action of alkali hydroxides on 1-phenylisoquinolinium methiodide and papaverinium methyl halides leads to the formation of 2-phenyl- $\alpha$ -naphthol and 6:7-dimethoxy-2-*mp*-dimethoxyphenyl- $\alpha$ -naphthol, which on oxidation yield binuclear quinones having the appearance of indigotin.<sup>79</sup>



The residual affinity of quinones is also manifested by the formation of additive compounds with certain inorganic chlorides. The following are representative examples of this series: *p*-benzoquinone stannic chloride,  $\text{C}_6\text{H}_4\text{O}_2, \text{SnCl}_4$  (red),  $\alpha$ -naphthaquinone antimonie chloride,  $\text{C}_{10}\text{H}_6\text{O}_2, 2\text{SbCl}_5$  (red),  $\beta$ -naphthaquinone stannic chloride (green), phenanthraquinone mercuric chloride,  $2\text{C}_{14}\text{H}_8\text{O}_2, \text{HgCl}_2$  (red).<sup>80</sup> Aromatic ketones behave similarly, and the following yellow compounds have been obtained, benzophenone antimonie chloride,



and benzil stannic chloride,  $(\text{COPh})_2, \text{SnCl}_4$ .

F. Kehrman refers the production of these compounds to the salt-forming capacity of quinonoid oxygen, and points out that he had previously shown that phenanthraquinone and chrysoquinone are dibasic substances forming two series of salts.<sup>81</sup>

An ingenious use of the properties of phenyliminoquinones has been made in the study of the tri-, tetra-, penta-, hepta-, and octa-bromo-

<sup>78</sup> W. Schlenk, *Annalen*, 1908, **363**, 313; *A.*, 1909, i, 36.

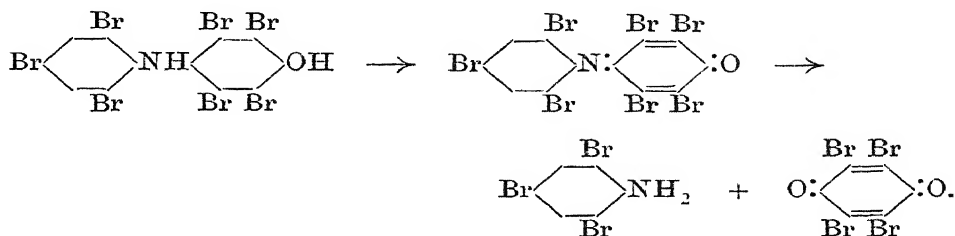
<sup>79</sup> H. Decker, *ibid.*, **362**, 305; *A.*, i, 806.

<sup>80</sup> K. H. Meyer, *Ber.*, 1908, **41**, 2018; *A.*, i, 731.

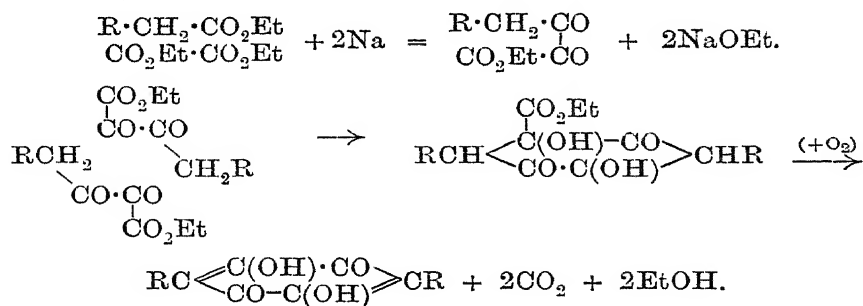
<sup>81</sup> *Ber.*, 1908, **41**, 3396; *A.*, i, 993.

derivatives of *p*-hydroxydiphenylamine. In each case, oxidation with chromium trioxide gives rise to the corresponding quinoneanil (phenyliminoquinone), the colour of which becomes more intense as the proportion of bromine increases, the shades varying from scarlet to a purple so dark as to appear black.

These substances readily undergo hydrolysis, so that the number of bromine atoms present in each ring, and, in some cases, also their orientation, are readily ascertained : <sup>82</sup>



An extremely interesting synthesis of quinones from straight-chain compounds has been effected by a modification of the process for producing ethyl alkyloxalacetates. A mixture of ethyl oxalate and an ester of a monobasic fatty acid is treated with sodium instead of sodium ethoxide, when a hydroxyquinone derived from a *p*-dialkylbenzene is produced :

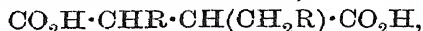


Atmospheric oxygen intervenes in the last step of this condensation, which takes place so readily that it may be employed as a lecture experiment to demonstrate the formation of a coloured quinone from colourless, comparatively simple, aliphatic esters. In the foregoing scheme, R may be methyl, ethyl, *isopropyl*, *n*-butyl, phenyl, or benzyl. These hydroxyquinones are yellow, whereas their alkali salts are bluish-violet.

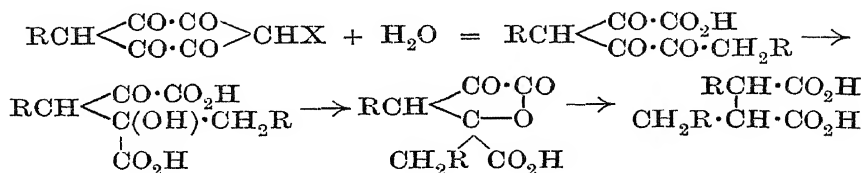
Equally noteworthy is the unique hydrolysis of these dihydroxydialkylbenzoquinones under the influence of boiling aqueous alkali

<sup>82</sup> A. E. Smith and K. J. P. Orton, *Trans.*, 1908, **93**, 314.

hydroxides, when the ring structure disappears with the production of symmetrically disubstituted succinic acids,



which are always obtained in their two stereoisomeric modifications, so that in some cases the reaction may with advantage be employed in the preparation of these isomerides. In this hydrolysis, the hydroxy-quinones react in their tautomeric form :

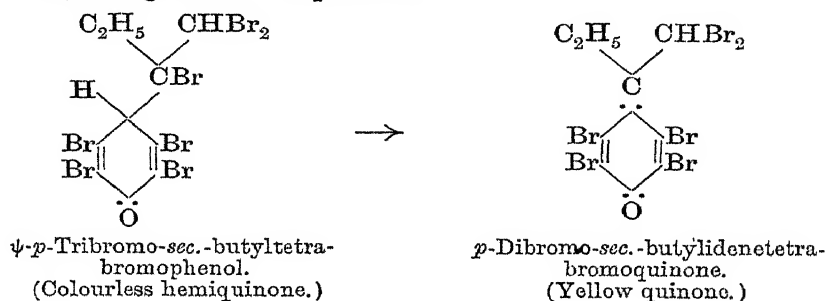


The triketocarboxylic acid containing an  $\alpha$ -diketonic group undergoes the benzoic acid change to a dicarboxylic acid which condenses to a lactonecarboxylic acid ; this compound then takes up water and loses carbon dioxide to form the disubstituted succinic acid.

The penultimate product, the lactonecarboxylic acid, was in one instance prepared by an independent method and shown to undergo the last step in the hydrolysis under the influence of alkali hydroxides.<sup>83</sup>

In connexion with the production of quinones, reference may be made to the more recent of Zincke's long series of researches on the chlorination and bromination of phenols.<sup>84</sup>

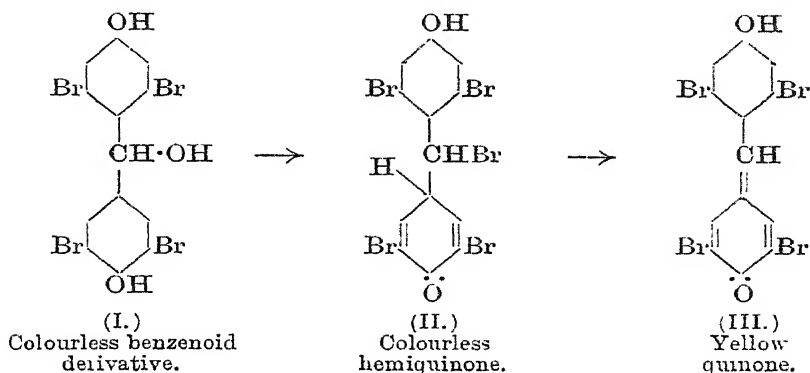
Di-*p*-hydroxydiphenylmethylethylmethane yields a tetrabromo-derivative,  $\text{HO} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CMeEt} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{OH}$ , which on further bromination is resolved into *s*-tribromophenol and the  $\psi$ -hexabromide of *p*-*sec*.-butylphenol ; at 100° a  $\psi$ -heptabromide is produced. These  $\psi$ -bromides, which unlike the less brominated phenols are insoluble in aqueous alkali hydroxides without decomposition, readily lose hydrogen bromide when treated with sodium acetate or sodium carbonate, and give rise to quinones :



<sup>83</sup> F. Fichter, *Annalen*, 1908, 361, 363 ; *A.*, i, 658.

<sup>84</sup> T. Zincke and J. Goldemann, *ibid.*, 362, 201 ; *A.*, i, 780 ; T. Zincke and E. Birschel, *ibid.*, 221 ; *A.*, i, 781.

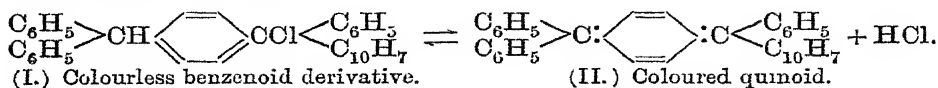
The tetrachloro- and tetrabromo-dihydroxybenzhydrols (I), when treated with hydrogen chloride and hydrogen bromide respectively, yield the  $\psi$ -pentachloro- and  $\psi$ -pentabromo-dihydroxydiphenylmethyl chloride and bromide (II). These halides, when shaken with aqueous acetone, lose hydrogen halide and furnish the tetrachloro- and tetrabromo-hydroxybenzylidenequinones (III).



These examples suffice to show the close relationship between the appearance of colour and the development of the complete quinonoid configuration. Of interest in this connexion is the preparation of coloured hydrocarbons of the quinodimethane series, of which the following synthesis is an example :

Benzoyltriphenylmethane,  $\text{COPh} \cdot \text{C}_6\text{H}_4 \cdot \text{CHPh}_2$ , when subjected to the Grignard reaction with magnesium  $\alpha$ -naphthyl bromide, yields a substituted benzhydrol,  $\text{HO} \cdot \text{CPh}(\text{C}_{10}\text{H}_7) \cdot \text{C}_6\text{H}_4 \cdot \text{CHPh}_2$ , from which *p*-benzhydryldiphenyl- $\alpha$ -naphthylmethyl chloride (I),

$\text{Cl} \cdot \text{CPh}(\text{C}_{10}\text{H}_7) \cdot \text{C}_6\text{H}_4 \cdot \text{CHPh}_2$ ,  
is readily obtained by the action of hydrogen chloride. This chloride, when heated with quinoline, loses hydrogen chloride, giving rise to the orange-red hydrocarbon, triphenyl- $\alpha$ -naphthylquinodimethane (II). This hydrocarbon absorbs halogen halide, regenerating the chloride (I). These changes constitute a reversible reaction, which may be represented as follows : <sup>85</sup>



Recently several methods of oxidising aromatic hydrocarbons to quinones have been patented, based on the indirect employment of electrolytic methods. For example, manganic alum, produced electrolytically from an aqueous solution of manganous and ammonium

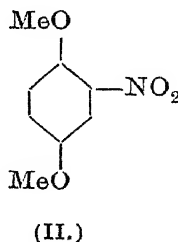
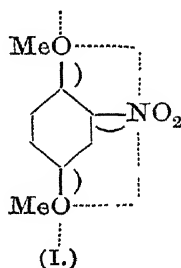
<sup>85</sup> A. E. Tschitschibabin, *Ber.*, 1908, **41**, 2770; *A.*, i, 872.



sulphates, is recommended for oxidising naphthalene, anthracene, and phenanthrene to their respective quinones.<sup>86</sup>

### *Colour and Constitution.*

Contributions to the study of the relation of colour to structure have again been very numerous, and in several of these a comparison has been made between colour and fluorescence. Starting from the much-discussed case of nitroquinol dimethyl ether, an examination of a large number of coloured and fluorescent substances<sup>87</sup> has shown that the colour of the light emitted in fluorescence is quite commonly dependent on the solvent employed. The fluorescent band of the solid substance lies furthest towards the ultra-violet, then follow the solutions in indifferent solvents, then those in dissociating solvents, the fluorescence of the vapour exposed to Tesla-radiation lying nearest to the red. This is true even of compounds in which it is impossible to assume a change of constitution to be brought about by dissociating solvents. Changes of colour in general run parallel with fluorescent changes. The theory of partial valencies is invoked in explanation of these facts. Considering the ordinary statical formulæ as representing an ideal constrained state of the molecule, the solid substance and its solutions in indifferent solvents are supposed to approach most nearly to this, whilst a greater freedom of the partial valencies is possible in dissociating solvents and in the state of vapour. Nitroquinol dimethyl ether is then written in the form (I), the

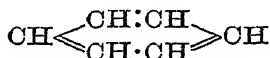


formula (II) representing the ideal limiting condition. The paler the colour of the solution the more nearly the molecule approaches to the limiting condition, which is, however, never completely attained. *m*-Nitrodimethylaniline is a good example of a compound showing variable fluorescence. The results are unfavourable to the assumption of a quinonoid structure. The influence of solvents in modifying the direction of the lines of force which constitute the partial valencies is illustrated and discussed.

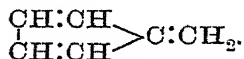
<sup>86</sup> D.R.-P. 189178; *A.*, i, 350.

<sup>87</sup> H. Kauffmann, *Ber.*, 1908, **41**, 4396; *A.*, 1909, i, 96.

Somewhat different results have been reached by a very exhaustive study of the triphenylmethane (or "tritane") series.<sup>88</sup> It is shown that the parallel between colour and fluorescence must not be pressed too far. Simple ring compounds, such as benzene, are fluorescent, although the emitted light lies in the ultra-violet portion of the spectrum, and by substitution, or by the juxtaposition of rings, the oscillations causing fluorescence may be so far retarded as to enter the visible region. Thus anthracene has a distinct fluorescence. The production of colour occurs in a quite different way. The replacement of hydrogen in benzene by substituents, however heavy, is quite incapable of retarding the oscillations so as to bring the ultra-violet absorption of benzene into the visible region. The colour of benzene derivatives is brought about, not by the shifting of a previously existing ultra-violet band towards the red, but by the production of a new band or bands, and for this a definite arrangement of conjugated double linkings is required. The author considers the key to the problem to be given by a comparison of benzene with its isomeride, fulvene. In both compounds, the number of carbon and hydrogen atoms, and of double linkings is the same, and only the disposition of the latter is altered.

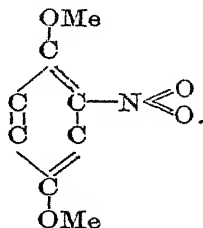


Benzene (colourless).



Fulvene (coloured).

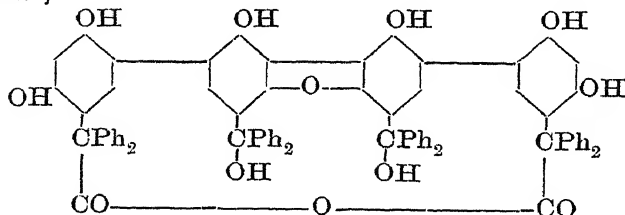
From a comparison of a large number of coloured substances, the author concludes that there is only one true organic chromophore, namely, the grouping  $\begin{array}{c} \text{R} \quad \text{R} \quad \text{R} \\ \parallel \quad \parallel \quad \parallel \\ \text{A} - \text{A} - \text{A} \end{array}$ , with three double linkings. This grouping is not, however, sufficient in itself to bring about colour, but requires some further condition (most frequently the closing of a ring) to produce visible colour. The reason for this is that the double linkings must first be brought into a definite relative position before the rhythmic oscillations which cause colour can be set up. It will be observed that nitroquinol dimethyl ether contains the required grouping, together with the ring :



<sup>88</sup> H. von Liebig, *Annalen*, 1908, 360, 128; *A.*, i, 445.

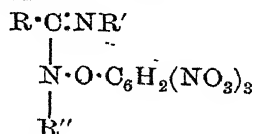
Coloured solutions of such simple coloured substances as diacetyl must contain polymerised molecules in order to render the above grouping possible, an assumption for which there is good evidence.

Fluorescence is explained as due to a pulsating interchange of double linkings in rings, brought about by impinging light-waves. The tritane derivatives examined ranged from the colourless triphenylmethane, through compounds exhibiting both colour and fluorescence, to the penta- and hepta-acetyl derivatives of the complicated hydroxy tritanol ether,

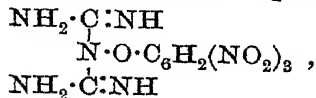


which exhibit colour, fluorescence, and pleochroism, a property hitherto only possessed by chlorophyll amongst colouring matters.

The picryl ethers of certain amidines have been noted as showing a remarkably strong fluorescence, although nitro-groups generally hinder the appearance of this property.<sup>89</sup> The non-fluorescent 1:2-diphenyl-3-benzyloxyamidine yields a highly fluorescent ether, and the same is found to be true of other non-fluorescent imide bases. The essential grouping appears to be



and that the residual affinity of the nitro-groups, acting in the direction of the imino-nitrogen atom, is connected with the property is suggested by the fact that the salts of the same imides with heavy metals, which are certainly internally complex, are highly coloured. The phenyl groups are not necessary, since picryl diguanide,



is also fluorescent. The effect is attributed to internal oscillations of linking in the molecule.

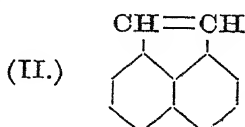
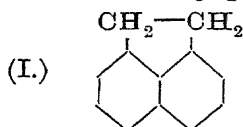
Pulsations of the ring-system of benzene were invoked to explain the absorption of benzene in the ultra-violet,<sup>90</sup> it being shown that the

<sup>89</sup> H. Ley, *Ber.*, 1908, 41, 1637; *A.*, i, 570.

<sup>90</sup> E. C. C. Baly, W. H. Edwards, and A. W. Stewart, *Trans.*, 1906, 89, 514.

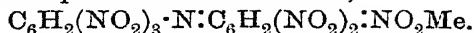
number of absorption bands corresponded with the number of distinct modes of deformation of the ring. This hypothesis has now been put to a severe test by the examination of compounds containing more than one ring.<sup>91</sup> Naphthalene itself has three bands in the ultra-violet, one of which is attributed to the benzenoid ring, and the other two to the conjugation of this with the ethylenic linkings of the second ring. When this second ring is entirely reduced in 1:2:3:4-tetrahydronaphthalene, only the one benzenoid band is observed. In 1:4:5:8-tetrahydronaphthalene, the two rings are exactly alike, and the symmetrical arrangement resembles that of *p*-xylene, and the two spectra are consequently almost identical.

A similar spectrum is given by acenaphthene (I), whilst acenaphthylene (II) has, in addition, bands due to the influence of the double linking outside the ring, producing colour.



The complete absorption spectra of a number of compounds containing nitro- and nitroso-groups have been examined, and the position of the band is found to depend on the nature of the atom to which the group is attached.<sup>92</sup> Dinitro-paraffins form both coloured and colourless solutions, the spectra of the former, and of the alkaline salts of these compounds, being unlike those of *aci*-mononitro-salts,  $R \cdot CH \cdot NO_2M$ . They are therefore assumed to contain an isomeric modification with quinonoid grouping,  $R \cdot C \begin{smallmatrix} \text{NO} \\ \text{NO(OM)} \end{smallmatrix} \text{O}$ , producing colour, in equilibrium with the colourless form.<sup>93</sup>

In continuation of the work on the strongly-coloured *aci*-ethers of nitrophenols, a dark violet *aci*-ether of hexanitrodiphenylamine has now been prepared<sup>94</sup> from the violet silver salt. It is therefore assumed to have the quinonoid constitution,



The fact that halogen-phenols, in which it is difficult to assume a quinonoid rearrangement, form both coloured and colourless silver salts<sup>95</sup> points to the necessity of further investigation of this kind of isomerism, and an interesting case of the same kind has been recently discovered.<sup>96</sup>

<sup>91</sup> E. C. C. Baly and W. B. Tuck, *Trans.*, 1908, 93, 1902.

<sup>92</sup> E. C. C. Baly and C. H. Desch, *ibid.*, 1747.

<sup>93</sup> E. P. Hedley, *Ber.*, 1908, 41, 1195; *A.*, i, 382.

<sup>94</sup> A. Hantzsch and S. Opoloski, *ibid.*, 1745; *A.*, i, 526.

<sup>95</sup> *Ann. Report*, 1907, 114.

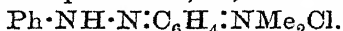
<sup>96</sup> O. Dimroth and O. Dienstbach, *Ber.*, 1908, 41, 4055; *A.*, 1909, i, 62.

4-Oximino-1-phenyl-5-triazolone,  $\text{NPh} \begin{array}{c} \text{N}=\text{N} \\ \diagdown \quad \diagup \\ \text{CO} \cdot \text{C} \cdot \text{N} \cdot \text{OH} \end{array}$ , forms three series of salts, yellow, red, and green, of which the red is usually the stable form, although the red silver salt is labile, and passes into the stable green modification. Further, the benzoyl and acetyl derivatives, which no longer contain a labile atom, also occur in red and yellow modifications, of which the latter is the stable form. That the case is one of chemical isomerism, and not merely of polymorphism, is shown by the fact that the red benzoyl derivative dissolves in chloroform to a deep red solution, which, however, immediately becomes yellow. Concentrated solutions are orange, and contain the two modifications in equilibrium.

Many aminoazo-compounds are known to form two series of differently coloured salts. The orange salts<sup>97</sup> resemble azobenzene in colour and must have the azo-constitution,



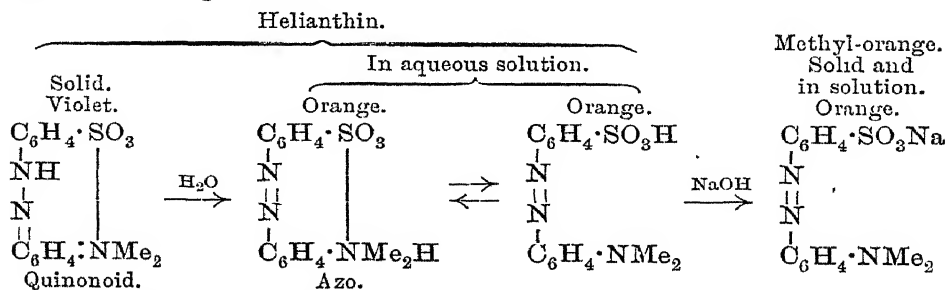
whilst the violet salts are quinonoid, as, for example,



The solid orange salts are usually labile, and are converted into the violet salts on heating, or, in some cases, on rubbing.

The violet salts were proved to be unimolecular in solution. Indifferent solvents favour the violet modification, whilst the orange modification persists in alcohol, ether, or acetone. The solutions in concentrated sulphuric acid are all yellow, and resemble azobenzene.

The same colour relationships appear in the aminoazobenzene-sulphonic acid series, and the colour-changes in helianthin and methyl-orange have therefore received a similar explanation,<sup>98</sup> the intermediate formation of an internal azo-salt being assumed, as represented in the following scheme :



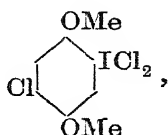
Azomethines are of interest from their analogy to azo-compounds. Since the simplest azomethines and their ethers are colourless, whilst their hydrochlorides show an absorption band in the blue region of the

<sup>97</sup> A. Hantzsch and F. Hilscher, *Ber.*, 1908, **41**, 1171; *A.*, i, 484.

<sup>98</sup> A. Hantzsch, *ibid.*, 1187; *A.*, i, 469.

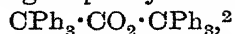
spectrum, it has been concluded<sup>99</sup> that the latter are quinonoid oxonium salts, the simplest ethyl ether hydrochloride, for instance, having the formula  $C_6H_5 \cdot CH_2 \cdot N : C_6H_4 \cdot O < \begin{smallmatrix} Et \\ Cl \end{smallmatrix}$ .

A recent observation<sup>1</sup> is of interest as showing that the possession of residual affinity may suffice to give chromophoric properties to a group of compounds, even when no ethylenic linking is present. Iodochlorides, such as



are strongly coloured red. Hitherto all chromophores attached to the benzene ring have contained a double bond.

The investigations into the constitution of triphenylmethyl, which derive their interest mainly from their bearing on such problems as those just discussed, have added little to the knowledge summarised in last year's Report (p. 118). The hexaphenylethane formula seems well established for the solid substance. An attempt to prepare hexaphenylethane by heating triphenylmethyl triphenylacetate,



yielded only an amorphous product, together with triphenylmethane. The product obtained from Gomberg's triphenylmethyl, and formerly supposed to be hexaphenylethane,<sup>3</sup> is now<sup>4</sup> proved to be *p*-benzhydryltetraphenylethane,  $CHPh_2 \cdot C_6H_4 \cdot CPh_3$ , by its synthesis from *p*-benzoyltriphenylmethane, which reacts with magnesium phenyl bromide to form *p*-benzhydryltriphenylcarbinol; condensation with aniline hydrochloride and elimination of the amino-group then gives Gomberg's compound, which is thus an isomeride, and not a polymeride, of triphenylmethyl. The preparation of the latter compound from the magnesium chloride has been improved,<sup>5</sup> and the existence of isomeric modifications of magnesium triphenylmethyl chloride has been defended against the criticisms of Tschitschibabin. The existence of both a coloured and a colourless modification in solutions of triphenylmethyl is inferred from the disappearance of the yellow colour on shaking with air, the yellow modification being the more readily oxidised.<sup>6</sup> On removing the peroxide by filtration, the colourless

<sup>99</sup> F. G. Pope, *Trans.*, 1908, **93**, 532, 1914.

<sup>1</sup> H. Kauffmann, *Ber.*, 1908, **41**, 4413; *A.*, 1909, i, 95.

<sup>2</sup> R. Anschütz, *Annalen*, 1908, **359**, 196; *A.*, i, 331.

<sup>3</sup> M. Gomberg, *ibid.*, 1908, **36**, 376; *A.*, 1908, i, 244.

<sup>4</sup> A. E. Tschitschibabin, *Ber.*, 1908, **41**, 2421; *A.*, i, 624.

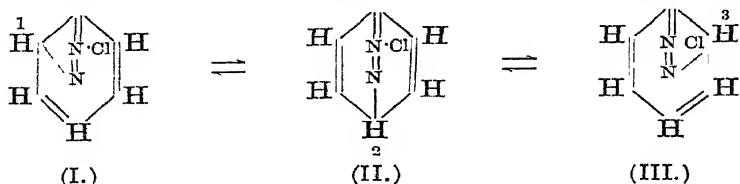
<sup>5</sup> J. Schmidlin, *ibid.*, 1908, **41**, 423, 426; *A.*, i, 150.

<sup>6</sup> *Ibid.*, 2471; *A.*, i, 623.

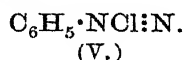
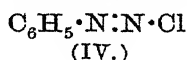
filtrate again becomes yellow, an ethereal solution in equilibrium at the ordinary temperature containing about ten times as much of the colourless as of the coloured form. Lowering the temperature favours the production of the colourless modification. The theoretical explanation of these facts has made little progress since last year.

### *Aromatic Diazo-compounds.*

In last year's Report reference was made to a new formula (II) for diazonium salts advocated by Cain,<sup>7</sup> which was put forward to account



for the following facts: (1) The property of giving rise to diazonium derivatives is confined to the aromatic primary amines, and is not possessed by the bases of the fatty series or fully saturated ring series; (2) the facility with which nitrogen is eliminated from diazonium salts suggests an unstable double linking  $\text{>C:N}$ , rather than the single linking  $\text{>C}\cdot\text{N}$ , assumed to be present in the Kekulé (IV) and Blomstrand (V) formulæ,



An ortho-quinonoid configuration would, however, afford an equally simple explanation of these facts, and accordingly it has recently been suggested that diazonium salts might appropriately be represented by a dynamic formula, in which the valency of the triad nitrogen atom in the foregoing static ortho- and para-quinonoid formulæ (I, II, III) is directed successively to the carbon atoms marked 1, 2, and 3, but is not held continuously by any one of them. This extremely labile condition of the oscillating linking would account for the production of hydrazines rather than diamines on reduction.<sup>8</sup>

These views on the structure of diazonium salts have been vigorously attacked by Hantzsch,<sup>9</sup> who contends that if diazonium salts are hemi-*p*-quinonoids, as represented by Cain's formula, then on reduction they should yield *p*-diamines and not hydrazines. He also repudiates the suggestion of a dynamic formulation, contending that

<sup>7</sup> *Ann. Report*, 1907, 120.

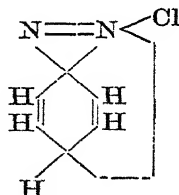
<sup>8</sup> G. T. Morgan and F. M. G. Micklethwait, *Trans.*, 1908, 93, 617.

<sup>9</sup> *Ber.*, 1908, 41, 3532.

this hypothesis, instead of obviating the difficulty of explaining the production of hydrazines rather than diamines, increases it twofold inasmuch as a mixture of ortho- and para-diamines should result from the reduction of such a compound. This view of the matter, however, involves the assumption that the properties of a substance with a dynamic structure are simply those of the tautomerides representing the extreme phases of the molecular oscillation. It is at least conceivable that the predominant properties of the compound might be those of the intermediate phase or phases. This conception, when applied to diazonium salts, furnishes a reason for the formation of hydrazines as the main products of reduction.

Cain,<sup>10</sup> who has replied to Hantzsch's criticisms of his formula, points out that there is experimental evidence for the view that reducing agents would break the unstable linking,  $>\text{CH}\cdot\text{N}$ , rather than the more stable azo-bond,  $-\text{N}:\text{N}-$ . He also calls attention to Hantzsch's admission that the existence of aromatic diazonium salts and the non-formation of such derivatives of the aliphatic amines point to some interaction of the residual affinities of the aromatic nucleus with the unsaturated diazonium complex. He maintains that this connexion is more definitely expressed by his quinonoid formula than by the vague addition made by Hantzsch to the Blomstrand configuration formula and expressed by the dotted line in the following formula,  $\text{C}_6\text{H}_5\cdot\text{N}_2\text{X}$ .

Euler,<sup>11</sup> who advocates another para-quinonoid formula for diazonium salts,



also lays stress on Hantzsch's admission of the imperfection of the Blomstrand formula (V.).

Although these controversial matters require further experimental evidence for their complete elucidation, yet this discussion has served the useful purpose of recalling attention to the important fact, so frequently overlooked, that the residual affinity of the aromatic nucleus is the determining factor both in the production of diazonium salts, and also in many other characteristic properties of aromatic compounds.

The study of the decomposition of diazonium salts in solutions of

<sup>10</sup> *Ber.*, 1908, 41, 4189; *A.*, 1909, i, 70.

<sup>11</sup> *Ibid.*, 3979; *A.*, 1909, i, 70.



varying strengths and at different temperatures has led to the following results.<sup>12</sup>

1. Dry<sup>13</sup> diazonium chlorides give the maximum value for the velocity of decomposition in aqueous solutions. Freshly prepared specimens decompose more slowly, and contain apparently traces of a protecting substance, the nature of which has not been elucidated.

2. Diazonium chlorides and bromides in solutions of the same concentration decompose at the same rate.

3. Increase in the concentration results in a small rise in the velocity of decomposition, which is somewhat greater with the bromides than with the chlorides. The velocity increases as the decomposition progresses, probably owing to the formation of halogenated hydrocarbons by the action of the liberated hydrogen halide.

4. Diazonium iodides decompose more rapidly than the chlorides or bromides, even in very dilute solutions.

5. Increase of concentration has but little effect on the velocity of decomposition of *p*-nitrobenzenediazonium chloride, and only in very concentrated solutions is any acceleration noticed. Neither strong nor weak acids have any protecting influence.

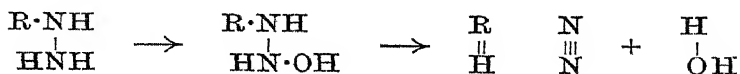
6. The less basic is the diazonium hydroxide set free by hydrolysis the more rapidly is the diazonium acetate decomposed in aqueous solution. Sodium chloride has a protecting influence on *p*-nitrobenzenediazonium acetate.

7. Nitrous acid decomposes diazonium salts, not catalytically, but by actual participation in the decomposition.

The experimental data on which this last generalisation is based agree with those formerly obtained by Cain,<sup>13</sup> and confirm his opinion that a solution of pure *p*-nitrobenzenediazonium chloride and another containing the same concentration of this salt with a trace of nitrous acid sufficient to give the starch-iodide test decompose with equal velocities under similar conditions of temperature.<sup>14</sup>

A study of the oxidation of primary aromatic hydrazines has led to a method of converting these substances quantitatively into the diazonium salts, from which they were obtained by reduction.

In the first place, the oxidation of these hydrazines with copper, silver, and mercuric oxides leads to the deposition of the corresponding metal, with the liberation of nitrogen and the formation of a hydrocarbon :



<sup>12</sup> A. Hantzsch and K. J. Thompson, *Ber.*, 1908, **41**, 3519; *A.*, i, 1021.

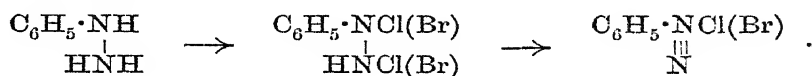
<sup>13</sup> *Ibid.*, 1905, **38**, 2511; *A.*, 1905, i, 724.

<sup>14</sup> *Ibid.*, 1908, **41**, 4186; *A.*, 1909, i, 70.

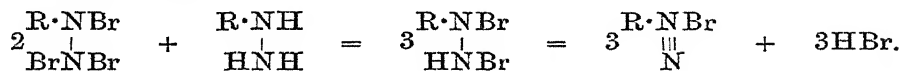
Manganese and lead dioxides give similar results, and potassium permanganate and hydroxide furnish benzene, azobenzene, and diphenyl.

The oxidation proceeds most smoothly with alkaline potassium chromate, when a practically quantitative yield of nitrogen and hydrocarbon is produced.<sup>15</sup>

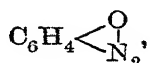
Although the foregoing experiments give no indication of the formation of diazonium salts, yet it has been found possible to obtain these compounds in excellent yield by introducing chlorine or bromine into an alcoholic solution of the hydrazine at temperatures below  $-20^{\circ}$ . This mode of procedure gives the solid diazonium salt, although a solution of the same can be obtained in glacial acetic acid by adding chlorine or bromine at  $0^{\circ}$ .<sup>16</sup>



A more convenient method of obtaining the solid diazonium bromide is first to prepare its perbromide by adding bromide to the aqueous solution of the diazonium salt. The dry perbromide, when mixed with the corresponding hydrazine in cold alcohol, undergoes the following change:<sup>17</sup>



The ortho- and para-aminophenols can be diazotised to diazo-oxides,



but the ortho-aminonaphthols, on treatment with nitrous acid in the presence of mineral acids, undergo oxidation to  $\beta$ -naphthaquinone.

It has been found that these aminonaphthols and their sulphonic acids can be diazotised readily, providing that mineral acids are absent. A solution of 1-amino- $\beta$ -naphthol-4-sulphonic acid, sodium nitrite, and sodium chloride slowly deposits the cyclic diazo-derivative,

$\text{NaSO}_3\cdot\text{C}_{10}\text{H}_6 \begin{array}{c} \text{N} \\ \diagup \diagdown \\ \text{O} \end{array}^2$ , and this result is also obtained by treating the sulphonic acid at  $40-50^{\circ}$  with sodium nitrite, zinc sulphate, and zinc hydroxide; other metallic salts may be used instead of zinc sulphate.<sup>18</sup>

Although diazo-oxides can be obtained from ortho-, para-, and peri-aminophenols, diazoimines can be prepared only from ortho- and peri-

<sup>15</sup> F. D. Chattaway, *Trans.*, 1908, **93**, 270.

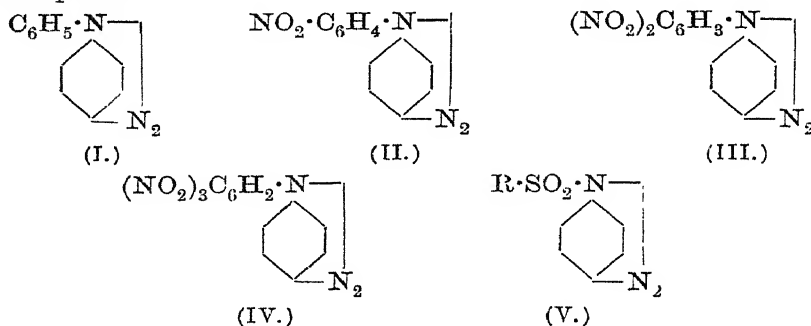
<sup>16</sup> *Ibid.*, 852.

<sup>17</sup> *Ibid.*, 958.

<sup>18</sup> D.R.-P. 189179, 195228, and 195322; *A.*, i, 231, 842.

diamines. The unsubstituted para-diamines do not give rise to diazoimines, although certain of their arylsulphonyl and aryl derivatives have been found to yield *p*-diazoimides and *p*-diazoimines of varying degrees of stability.

The simplest compound of this group is the explosive phenyl-*p*-phenylenediazoimine<sup>19</sup> (I) obtained by adding ammonia to the diazonium salt of *p*-aminodiphenylamine,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_6\text{H}_5$ . A series of increasingly stable *p*-diazoimines has been produced by gradually introducing nitro-groups into the phenyl nucleus of this base, so that when the trinitrophenyl (picryl) derivative is reached a *p*-diazoimine (IV) is produced, which is as stable as the *p*-diazoimides (V) obtained from the arylsulphonyl-*p*-diamines and mentioned in earlier reports.<sup>20</sup>



In the foregoing diagram these derivatives of the still unknown *p*-diazoiminobenzene are arranged in the order of their stability, which increases as the acidity of the substituent group becomes more pronounced. In spite of the great difference in stability, the members of this series all exhibit the two properties which are characteristic of *p*-diazoimino-derivatives. They combine additively with  $\beta$ -naphthol, and change quantitatively into the corresponding diazonium salt on treatment with cold concentrated mineral acids.<sup>21</sup>

#### *Hydrazones and Hydroxyazo-compounds.*

In considering the diazonium salts, special stress was laid on the fact that these are known only in the aromatic series. The compounds now under discussion may be either entirely aromatic or mixed aliphatic-aromatic derivatives.

Several important investigations on these substances have been published during the last year, and at last it seems likely that some agreement will be reached in regard to their constitution.

<sup>19</sup> *Annalen*, 1888, **243**, 282, and *Ber.*, 1902, **35**, 895.

<sup>20</sup> *Ann. Report*, 1906, 124 and 151.

<sup>21</sup> G. T. Morgan and F. M. G. Micklethwait, *Trans.*, 1908, **93**, 602.

The coupling of a diazonium salt with a phenol gives rise to an aromatic hydroxyazo-compound, whilst an aliphatic-aromatic azo-derivative results from the condensation of the diazonium salt with an aliphatic substance containing the group  $\cdot\text{CH}_2\cdot\text{CO}\cdot$ .

It is in the first place necessary to consider the constitution of the aliphatic and aromatic compounds concerned in these condensations.

Aliphatic compounds containing the above group tend to conserve this ketonic configuration, even although in certain reactions the dynamic enolic form comes into play.

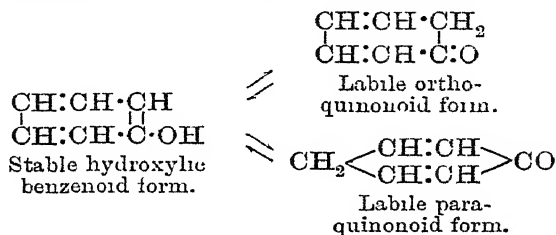


Stable ketonic form.

Labile enolic form.

In the aliphatic series the ketonic form is the more stable.

The converse holds with the phenols. Although it is frequently necessary to assume the intervention of the dynamic ketonic (quinonoid) form, this in the aromatic series is the labile condition, and whenever possible the phenol or its condensation product reverts to the stable hydroxylic (benzenoid) configuration.

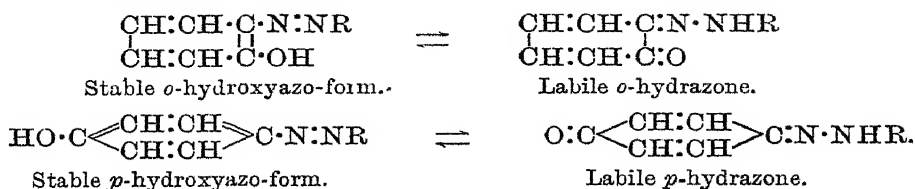


Recent experimental evidence is almost unanimous in demonstrating that these properties of the aliphatic diketones and aromatic hydroxy-derivatives are shared by the mixed and aromatic azo-compounds respectively, the aliphatic-aromatic derivatives tending always to acquire the hydrazone configuration, whilst the purely aromatic derivatives assume almost invariably the hydroxyazo-structure.

Aliphatic series :

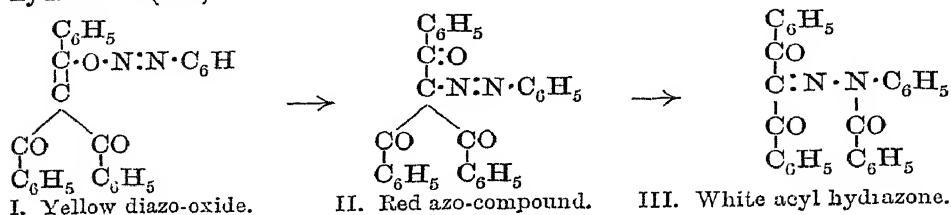


Aromatic series :

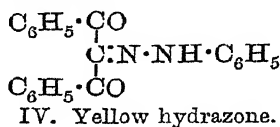


An investigation of the mechanism of the coupling of diazonium salts and aliphatic ketones has been carried out with tribenzoyl-methane, which reacts in its enolic form, since the first product is a diazo-oxide (I) containing the diazo-complex attached to the enolic oxygen. This is proved by the ease with which the diazo-group can be removed merely by treatment with  $\beta$ -naphthol or  $\alpha$ -naphthylamine,

This diazo-oxide passes successively into two isomerides, the first, a red azo-compound (II), and the last and most stable, a colourless hydrazone (III).



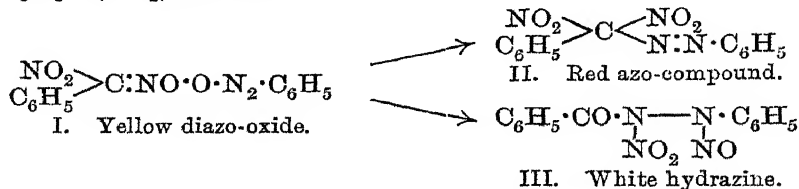
On hydrolysis, these three isomerides give the same products, namely, ethyl benzoate and the hydrazone (IV).



These results show that in the aliphatic series the final stable product is a hydrazone rather than an azo-compound.

When a very reactive group, such as nitroxyl, is present, the transformation of diazo-oxide into azo-compound and hydrazine derivative may occur simultaneously.

$\omega$ -Dinitrotoluene,  $\text{C}_6\text{H}_5 \cdot \text{CH}(\text{NO}_2)_2$ , and its homologues couple with diazonium salt in alkaline solutions, the first product being a diazo-oxide (I). This substance readily changes into two isomerides, a red azo-compound (II) and a white hydrazine derivative (III). In the initial coupling, the dinitro-compound is used in the form of its alkali salt,  $\text{C}_6\text{H}_5 \cdot \text{C}(\text{NO}_2)_2 \cdot \text{NO} \cdot \text{OK}$ .



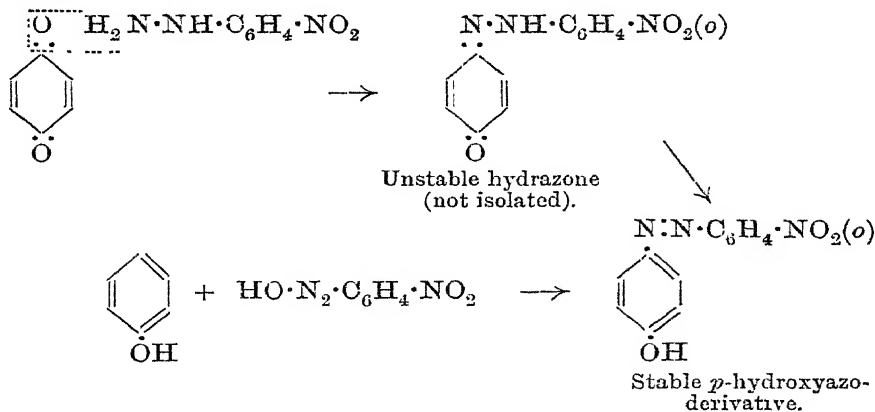
The constitution of the hydrazine derivative is shown by the action of water, which hydrolyses it first into nitric acid and nitrosobenzoyl-

phenylhydrazine,  $C_6H_5 \cdot CO \cdot NH \cdot N(NO) \cdot C_6H_5$ , this compound being finally decomposed into nitrous acid and *s*-benzoylphenylhydrazine.<sup>23</sup>

In the aromatic series the first product, the *O*-azo-derivative, or diazo-oxide, has also been isolated in a few cases where the velocity of transformation into the *C*-azo-derivative has been lessened by the presence of substituents in the reactive para-position. *p*-Bromobenzene-diazonium chloride and *p*-nitrophenol couple to give *p*-bromobenzene-diazo-4-oxynitrobenzene,  $C_6H_4Br \cdot N:N \cdot O \cdot C_6H_4 \cdot NO_2$ , which at 80° becomes transformed into its isomeride, the red *p*-bromobenzene-2-azo-4-nitrophenol,  $C_6H_4Br \cdot N:N \cdot C_6H_3(NO_2) \cdot OH$ .

Auwers<sup>24</sup> is inclined to regard these intermediate *O*-azo-derivatives as diazonium oxides, but inasmuch as they are produced only in the absence of acids stronger than acetic acid, it seems preferable to regard them as diazo-oxides,  $R \cdot N:N \cdot OY$ , analogous to the diazo-amines,  $R \cdot N:N \cdot NHY$ , which are formed under similar conditions and undergo the same change into *C*-azo-derivatives.

In 1907 W. Borsche succeeded in condensing *o*-nitrophenylhydrazine and 2:4-dinitrophenylhydrazine with *p*-benzoquinone and its homologues; the products were identical with the hydroxyazo-derivatives prepared by coupling *o*-nitrobenzenediazonium and 2:4-dinitrobenzenediazonium chlorides with phenol and its homologues.<sup>25</sup>



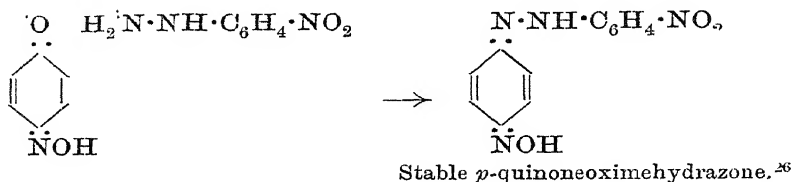
These condensations are of great interest, because the products are admittedly *p*-hydroxyazo-derivatives, formed by a process which ought to give rise to *p*-quinonehydrazones were it not for this tendency of the aromatic hydroxyl derivatives to conserve their hydroxylic structure.

<sup>23</sup> G. Ponzio and G. Charrier, *Atti R. Accad. Sci. Torino*, 1908, **43**, 303; *Gazzetta*, 1908, **38**, i, 526; *A.*, i, 482.

<sup>24</sup> *Ber.*, 1908, **41**, 4304; *A.*, 1909, i, 67.

<sup>25</sup> Borsche, *Annalen*, 1907, **357**, 171; *A.*, i, 66.

When a *p*-quinoneoxime is employed instead of the *p*-quinone itself in the foregoing condensation, then the primary product can be isolated.



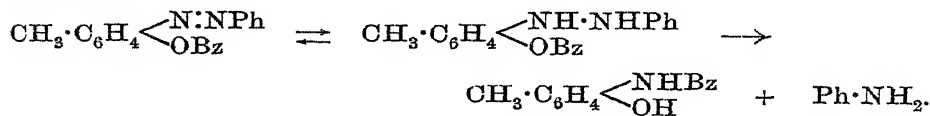
In this case the phenolic OH is replaced by NOH, so that the striving of the aromatic residue  $\text{>C<}$  to become  $\text{—C=O}$  is non-existent.

To the foregoing evidence may be added the closely related transformation of *p*-benzoquinonebenzoylphenylhydrazine into benzene-azo-*p*-phenyl benzoate under the influence of cold potassium hydroxide, already referred to in last year's Report (p. 126).

The production of  $\beta$ -benzeneazo- $\alpha$ -naphthyl benzoate from *as*-benzoylphenylhydrazine and  $\beta$ -benzoquinone simply means that the ortho-quinonehydrazones are even less stable than the paraquinonehydrazones and pass spontaneously into ortho-azo-derivatives.

The reduction of this  $\beta$ -benzeneazo- $\alpha$ -naphthyl benzoate has been compared with that of its isomeride,  $\alpha$ -benzeneazo- $\beta$ -naphthyl benzoate; the former gave benzanilide, aniline,<sup>27</sup> and *N*-benzoyl-2-amino- $\alpha$ -naphthol, whilst the latter yielded benzanilide, aniline, and *N*-benzoyl-1-amino- $\beta$ -naphthol.<sup>27</sup> The corresponding acetates behave similarly on reduction.

The reduction of benzene-*o*-azo-*p*-tolyl benzoate leads to the hydrazo-derivative, which, on heating in acetic acid, regenerates the azo-derivative and yields simultaneously *N*-benzoyl-*o*-amino-*p*-cresol and aniline:<sup>28</sup>



Benzanilide was never obtained in this reduction.

Bearing in view the fact that acyl groups readily shift from oxygen to nitrogen in aminophenols, Auwers considers that the foregoing

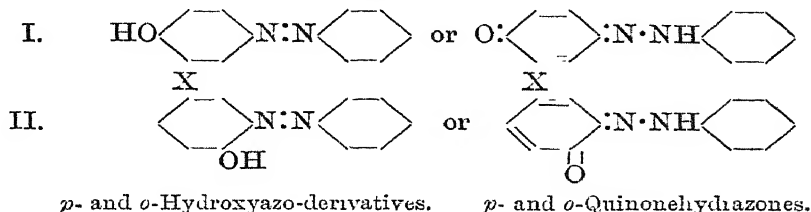
<sup>26</sup> There is evidence that this compound can assume the dynamic azo-form,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{OH}$ , in certain of its reactions, as, for example, oxidation (*loc. cit.*, p. 148).

<sup>27</sup> *Ber.*, 1908, 41, 403; *A.*, i, 228.

<sup>28</sup> K. Auwers and M. Eckardt, *Annalen*, 1908, 359, 336; *A.*, i, 480.

results favour the assumption that these esters are really azo-derivatives and not *o*-quinoneacylhydrazones.

Mercuric acetate was shown by Dimroth to condense with phenols and aromatic amines, entering the unsubstituted para- and ortho-positions with reference to the oxygen and nitrogen atoms respectively. On this account it has been employed in the study of hydroxyazo-compounds, for, as will be seen from the following formulæ, the number of mercuriacetate groups introduced into the azo-compound should be a criterion of its constitution :



Considered as an azo-derivative, the para-compound (I) should condense with not more than two mercuriacetate groups, whilst as hydrazone it should form a tri-substituted mercuriacetate. The ortho-compound (II), in its hydrazo-form, should also take up three mercuriacetate groups, but as an azo-derivative it should only condense with one molecule of mercuric acetate. In every case examined, the result corresponded with the hydroxyazo-structure, both in the ortho- and para-series.<sup>29</sup>

These results, like the other chemical evidence already cited, are all in favour of the view that the constitution of both ortho- and para-hydroxyazo-derivatives is what their usual designations imply, and that these substances have not in ordinary circumstances a hydrazone structure.

The spectroscopic evidence, as interpreted by Tuck, is, to a certain extent, against this view and in favour of the assumption that the ortho-hydroxyazo-compounds and their acyl derivatives have the quinonehydrazone constitution. Both Auwers and C. Smith, however, take exception to the comparisons instituted between the absorption curves, the former referring to the difference between the curve for benzoquinonebenzoylphenylhydrazone and those for a set of azo-derivatives, whilst the latter asserts that the curve for benzeneazo-*p*-tolyl benzoate, presumably a hydrazone, resembles that of benzeneazo-phenol, admittedly an azo-compound, more than that of the foregoing quinonehydrazone.

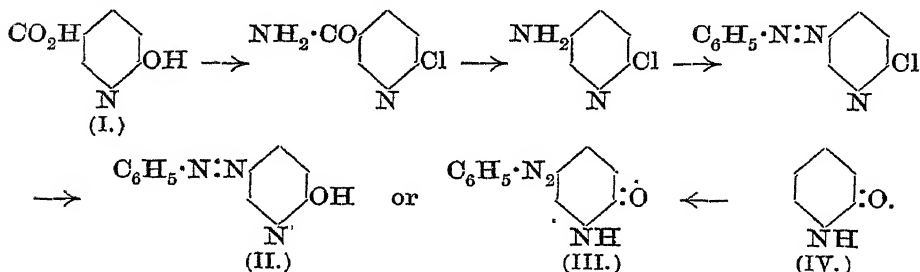
From the chemical evidence now available, it is permissible to deduce the general rule that a hydroxyazo-compound will be an azo-

<sup>29</sup> C. Smith and A. D. Mitchell, *Trans.*, 1908, 93, 842.



derivative or a hydrazone according as to whether its oxygenated generator is an enol or a ketone respectively.

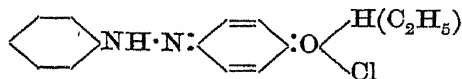
The case of 2-pyridone (IV) is of interest in this connexion, for this substance, which differs from the phenols in not giving the ferric chloride and nitrosoamine colorations and in not yielding acetyl and nitroso-derivatives, nevertheless forms an azo-compound, 5-benzene-azo-2-pyridone (II or III), with benzenediazonium chloride. The orientation of the substituents in this compound is established by the following series of operations, starting with 6-hydroxynicotinic acid (I), a substance of known constitution :<sup>30</sup>



This azo-derivative and the isomeric benzeneazo-3-hydroxypyridine merit further examination from the point of view of the constitution of hydroxyazo-compounds.

Although the balance of chemical evidence is in favour of the view that all aromatic hydroxyazo-derivatives have the azo-structure, the question of the nature of their salts with the mineral acids next arises. Some years ago Hewitt showed that, on nitration, benzeneazophenol itself behaves in accordance with its hydroxyazo-constitution,<sup>31</sup> and in this respect differed from its sulphate, which behaves as if it were a quinonehydrazone.

More recently it has been found that benzeneazophenol and its ethoxy-derivative, benzeneazophenetole, both admittedly azo-compounds, have similar absorption spectra in concentrated hydrochloric acid.<sup>32</sup> Accordingly the formula for the salts of benzeneazophenol must be applicable to the salts of benzeneazophenetole, and at the same time should account for the chemical properties of benzeneazophenol sulphate. After discussing several formulæ, Fox and Hewitt, who have prepared and examined spectroscopically the salts of a series of azophenols and their ethyl ethers, decide on the following structure :



<sup>30</sup> W. H. Mills and S. T. Widdows, *Trans.*, 1908, **93**, 1373.

<sup>31</sup> *Trans.*, 1900, **77**, 99.

<sup>32</sup> Tuck, *ibid.*, 1907, **91**, 450.

The compounds having this constitution are characterised spectroscopically by strong and persistent absorption in the yellow and green and chemically by behaving towards substituting agents as quinone-hydrazones.<sup>33</sup>

*Heterocyclic Rings containing Oxygen.*

*The Coumarin Group*—The coumarin condensation with malic acid or ethyl acetoacetate and the substituted phenols has been studied, the results showing that phenols containing alkyl, hydroxyl, or dialkyl-amino-groups in the positions indicated below give good yields of the corresponding coumarins.



Chlorine, as a substituent in these positions, has a similar effect, but to a less appreciable extent. The introduction of nitro-, carboxy-, or carbethoxy-groups prevents condensation.<sup>34</sup>

The condensation is affected considerably by the strength of the sulphuric acid employed; when 73 per cent. acid is used, a satisfactory yield of 4-methylcoumarin may be obtained from phenol and ethyl acetoacetate, otherwise the amount produced is very small.<sup>35</sup>

One of the most interesting, and still only partly explained, reactions of coumarin is its hydrolysis into coumarinic and *o*-coumaric acids. When treated with sodium ethoxide, coumarin and 7-methylcoumarin yield respectively ethyl *o*-coumarate and ethyl 4-methyl-*o*-coumarate. But under these conditions, 4:7-dimethylcoumarin, which contains one methyl group in the lactonic ring gives rise to more complex products, namely, 3-[2:5-dimethylhydrocoumarilyl]-4:7-dimethylcoumarin and 1-[2:5-dimethylhydrocoumarilyl]-2:5-dimethyldihydrocoumarone (II) respectively. A molecular proportion of the  $\beta$ -4-dimethylcoumaric acid produced by hydrolysis condenses with unaltered 4:7-dimethylcoumarin, and the product then undergoes rearrangement<sup>36</sup> and a coumaryl ring is produced (I). The second product is formed from the first by hydrolysis and loss of carbon dioxide.

The interaction of 4:6-dimethylcoumarin and sodium ethoxide leads to the production of similar products differing from compounds (I) and (II) only in the position of the methyl substituent in the benzene ring.

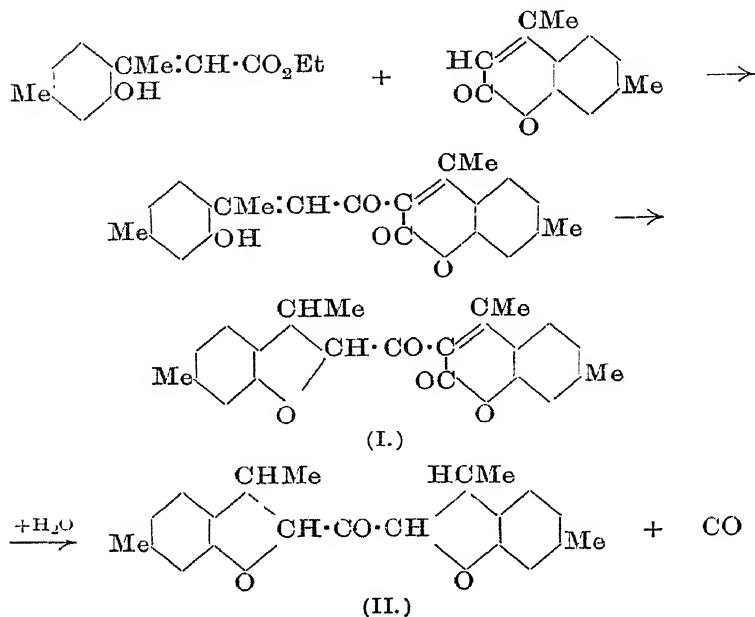
The reduction of coumarin with zinc dust and alkali hydroxide

<sup>33</sup> Fox and Hewitt, *Trans.*, 1908, **93**, 333.

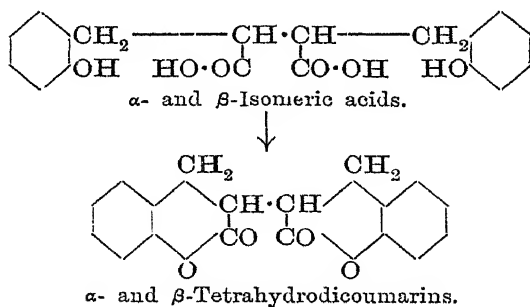
<sup>34</sup> A. Clayton, *ibid.*, 2018.

<sup>35</sup> F. Peters and H. Simonis, *Ber.*, 1908, **41**, 830; *A.*, i, 339.

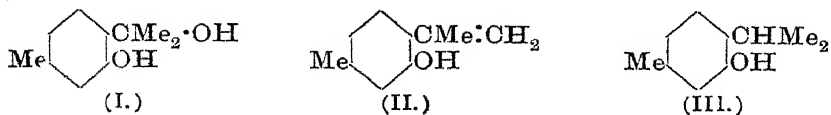
<sup>36</sup> K. Fries and W. Klostermann, *Annalen*, 1908, **362**, 1; *A.*, i, 820.



leads to melilotic acid as the main product, and, in addition, to two by-products, which are stereoisomeric  $\alpha$ - and  $\beta$ -tetrahydrodicoumaric acids, the isomerism of which resembles that of the symmetrically di-substituted succinic acids, and persists even when they are condensed into tetrahydrodicoumarins.

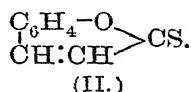
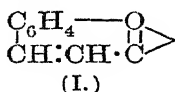


4:7-Dimethylcoumarin behaves differently on reduction, and gives rise to three products: 2-hydroxy-4-methylphenyldimethylcarbinol (I) (hydroxythymol), 2-hydroxy- $\alpha$ -4-dimethylstyrene (II), and thymol (III).



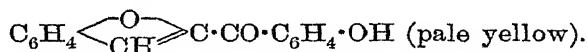
The second product also exists in a polymeric bimolecular form. These vinylphenols and their polymerides may be produced by distilling *o*-coumaric acid and its homologues under reduced pressure. The simplest member of the series, *o*-vinylphenol (*o*-hydroxystyrene), prepared from *o*-coumaric acid itself, readily polymerises. The bimolecular form is insoluble in alkali hydroxides, and becomes depolymerised when distilled under the ordinary pressure, although under 15 mm. it passes over unchanged.<sup>37</sup>

As the coumarins are colourless, and do not condense with either hydroxylamine or phenylhydrazine, whilst the thiocoumarins are yellow and yield oximes and phenylhydrazones, it has been suggested that coumarin has the modified structure (I), whilst thiocoumarin retains the configuration (II) generally attributed to coumarin :<sup>38</sup>



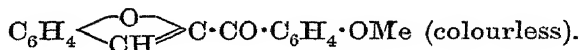
#### *The Flavone Group.*

The residue  $\cdot\text{C}:\text{C}:\text{CO}\cdot$  is often associated with the development of colour, and it may occur in compounds in four different ways; both  $\cdot\text{C}:\text{C}:$  and  $\cdot\text{CO}\cdot$  may be present in a ring, or both may occur in a chain, or one may be in the ring and the other in the chain. As the case of the ethyl linking in the ring ("cyclostatic") and the carboxyl group in the chain ("streptostatic") has not been studied, 1-hydroxybenzoylcoumarone, a compound having the required structure, has been synthesised from coumarilic chloride and phenol by the action of aluminium chloride,



The colour is absent from the alkyl derivatives. The methyl compound is synthesised in the following manner: salicylaldehyde and *p*-methoxybenzophenone give 2-hydroxy-4'-methoxychalkone,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , a yellow substance containing both chromophores in the streptostatic condition.

The acetate of this compound yields a dibromide, which on heating with alcoholic potash furnishes the required compound, 1-methoxybenzoylcoumarone,<sup>39</sup>



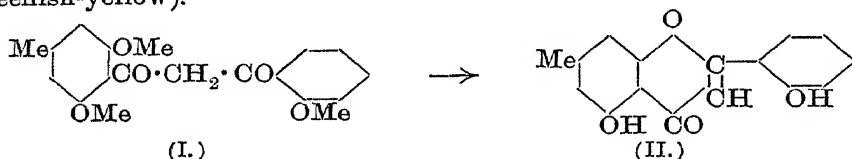
<sup>37</sup> K. Fries and G. Fickewirth, *Ber.*, 1908, **41**, 367; *A.*, i, 160.

<sup>38</sup> A. Clayton, *Trans.*, 1908, **93**, 524.

<sup>39</sup> F. Zwayer and S. von Kostanecki, *Ber.*, 1908, **41**, 1335; *A.*, i, 443.

The two chromophores are cyclostatic in the allied group of flavones, the hydroxy-derivatives of which exhibit colour, whereas their alkyl and acyl derivatives are colourless.

A series of flavones have been synthesised from oracetophenone dimethyl ether and the isomeric *iso*oracetophenone dimethyl ether, these ethers being produced by condensing acetyl chloride and orcinol dimethyl ether. One example of this synthesis will suffice to indicate the general method. Oracetophenone is condensed with methyl *o*-methoxybenzoate, yielding 2:6:2'-trimethoxy-4-methylbenzoylaceto-phenone (I); this intermediate product, when boiled with concentrated hydriodic acid, condenses into 1:2'-dihydroxy-3-methylflavone (II) (greenish-yellow).<sup>40</sup>



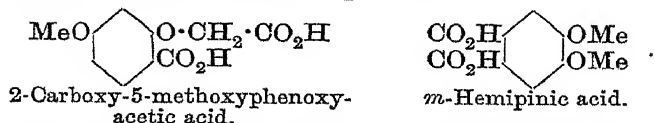
*Brazilin, Haematoxylin, and their Derivatives.*

The culminating point in a long series of researches on brazilin and hæmatoxylin has been reached this year with the demonstration of the constitution of these two substances and of the colouring matters, brazilin and hæmatein, into which they are converted by oxidising agents.

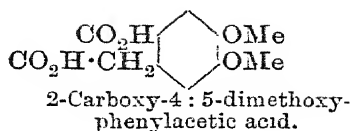
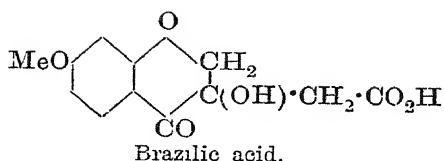
Brazilein and hæmatein are respectively the colouring matters of brazil-wood and logwood, both of which find extensive application in dyeing; they stand in the same relationship to brazilin and hæmatoxylin as *p*-benzoquinone does to quinol.

As in both cases the quinol derivative is more amenable to chemical treatment than the quinonoid substance, the problem of ascertaining the constitution of these substances has mainly been worked out with brazilin and hæmatoxylin. The former of these substances contains three, and the latter four, hydroxyl groups, and it was found advisable to protect these by methylation before systematically breaking down the compounds by oxidation.

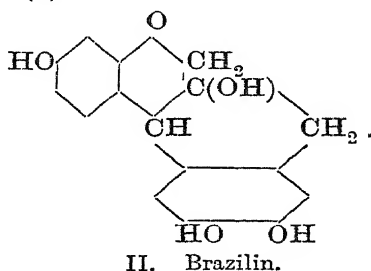
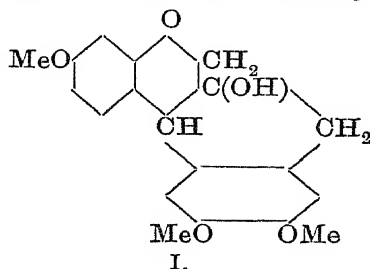
Trimethylbrazilin yields on treatment with potassium permanganate a number of acidic substances, all of which are of great importance in tracing out a skeleton formula for the parent substance. The following are two pairs of these oxidation products.



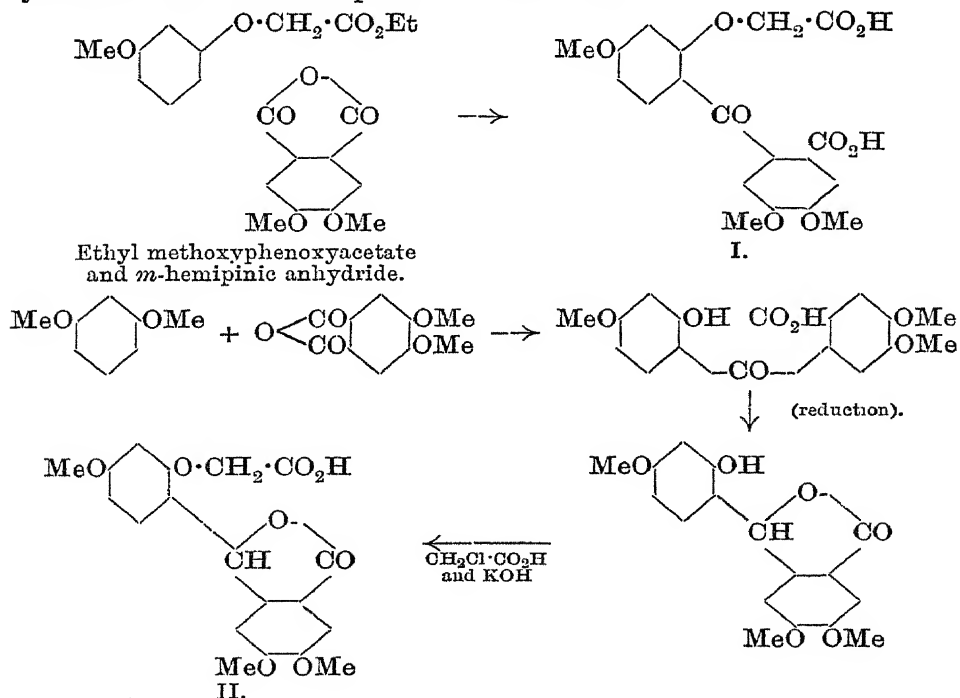
<sup>40</sup> J. Tambor, *Ber.*, 1908, 41, 787, 793; *A.*, i, 849, 858.



Bearing in mind that the empirical formula of trimethylbrazilin is  $C_{19}H_{20}O_5$ , a careful consideration of the oxidation products led to the graphical formula for trimethylbrazilin (I) :

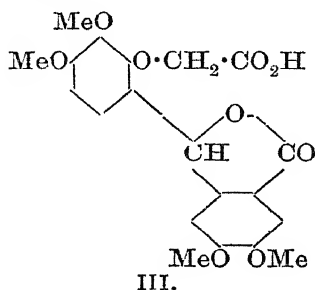


It will be seen that this constitution agrees with the formation of the foregoing oxidation products. In confirming this formulá, all the more important degradation products of trimethylbrazilin have been synthesised with the exception of brazilic acid.

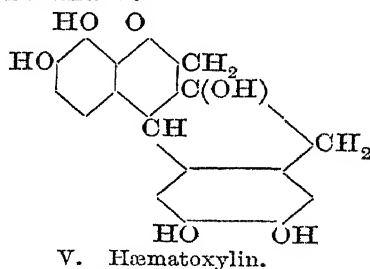
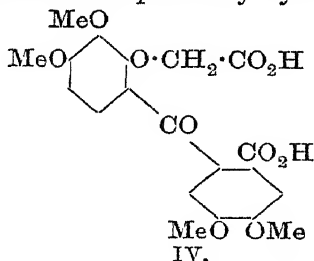


Of these syntheses, one of the most important is that of brazilinic acid (I), an oxidation product of trimethylbrazilin, which on reduction changes into the lactone (II) of dihydrobrazilinic acid. Both these substances have been synthesised in the manner indicated on p. 151.

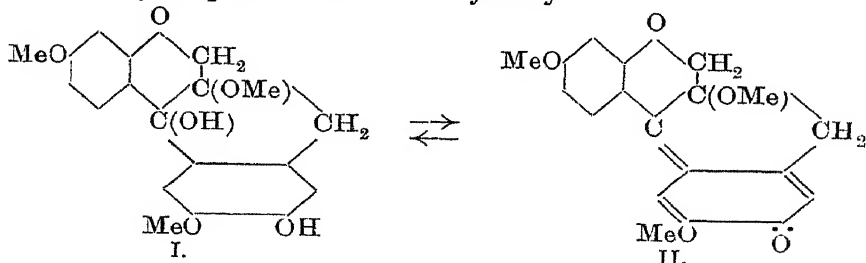
A similar synthesis, using *m*-hemipinic anhydride with pyrogallol trimethyl ether instead of the foregoing resorcinol dimethyl ether, led by a precisely comparable series of reactions to the lactone (III) of dihydrohæmatoxylinic acid :



a result which proves that hæmatoxylinic acid and hæmatoxylin must be represented respectively by formulæ IV and V.<sup>41</sup>

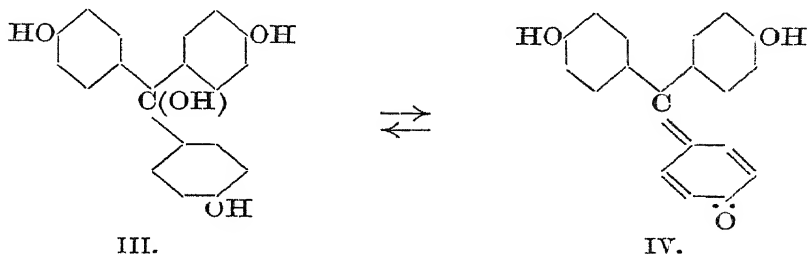


Brazilein has the empirical formula  $C_{14}H_{12}O_5 \cdot 2H_2O$ , losing water at  $130-140^\circ$ . On methylation it yields trimethylbrazilein (II) and tetramethyldihydrobrazileinol, the former of these on treatment with dilute aqueous potassium hydroxide becomes hydrated to trimethylbrazileinol (I); the tetramethyl derivative has the configuration (I) with methoxyl in place of the lower hydroxyl :

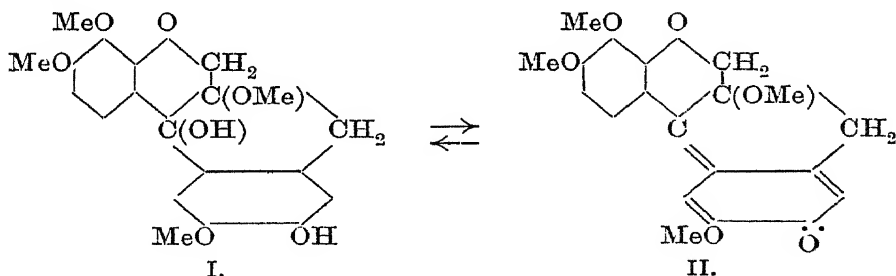


<sup>41</sup> W. H. Perkin, jun., and R. Robinson, *Trans.*, 1908, **93**, 489.

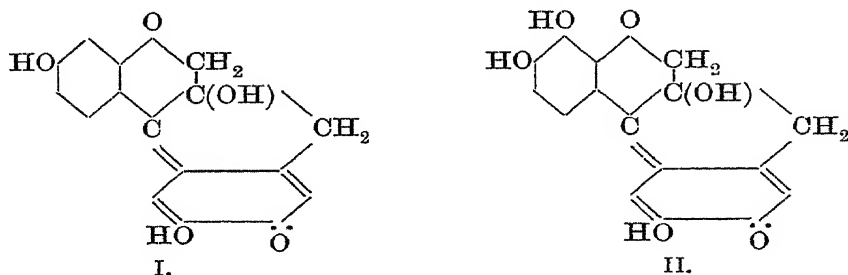
The trimethyldihydrobrazileinol is reconverted into trimethylbrazilein on heating, this reversible change being quite comparable with the change of trihydroxytriphenylcarbinol (III) into aurin (IV), and vice versa.



The close relationship existing between brazilin and hæmatoxylin indicates that hæmatein is hydroxybrazilein. The behaviour of hæmatein on methylation fully justifies this hypothesis. The colouring matter is converted into tetramethylhæmatein (II) and pentamethyldihydrohæmateinol; the former of these, when digested with dilute potassium hydroxide, is hydrated to tetramethyldihydrohæmateinol (I), a change which is reversed on heating :



These reactions, together with more confirmatory evidence, lead to the following formulæ for brazilin (I) and hæmatein (II) : <sup>42</sup>

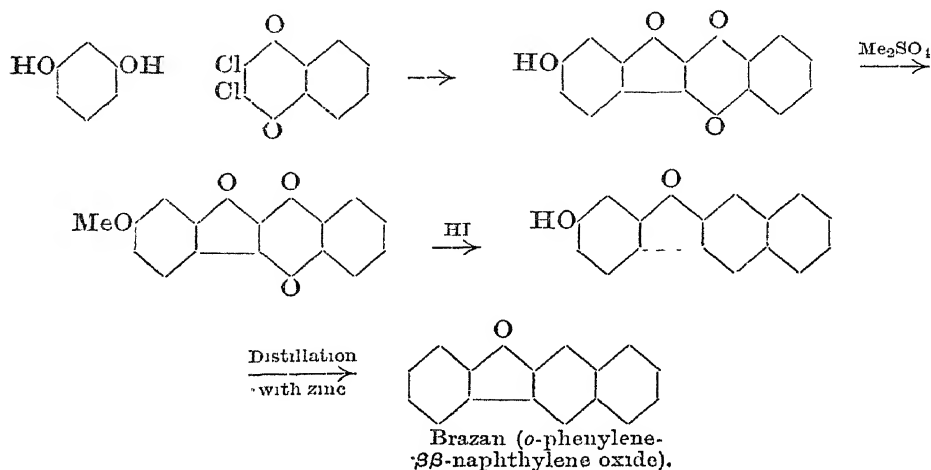


The synthesis of brazan, a substance obtained from brazilin, has

<sup>42</sup> P. Engels, W. H. Perkin, jun., and R. Robinson, *Trans.*, 1908, **93**, 1115.

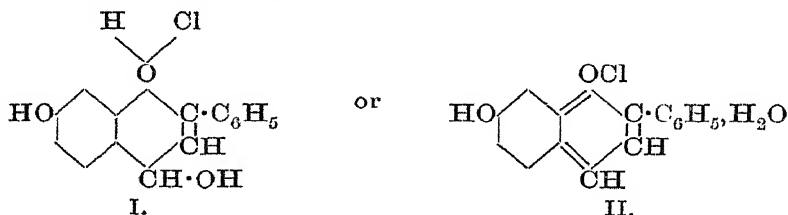


been effected in the following manner from resorcinol and 2 : 3-dichloro-naphthaquinone : <sup>43</sup>



### *Pyranol Salts.*

In connexion with the experiments on brazilin and hæmatoxylin, the synthesis and constitution of certain pyranol salts have been studied. As a typical example of these compounds, one may take the product obtained by condensing either resorcinol and benzoylacet-aldehyde or  $\beta$ -resorcylaldehyde and acetophenone. The hydrochloride of this pyranol contains an additional molecule of water, and may be represented by the following formulæ :

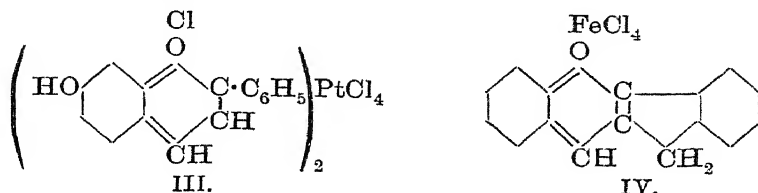


The balance of evidence is in favour of the second formula, which represents the salt as 7-hydroxy-2-phenylbenzopyranol(1 : 4)anhydrohydrochloride with one molecule of water of crystallisation. All the hydrochlorides examined could be formulated in this way, excepting that some contained even more water of crystallisation.

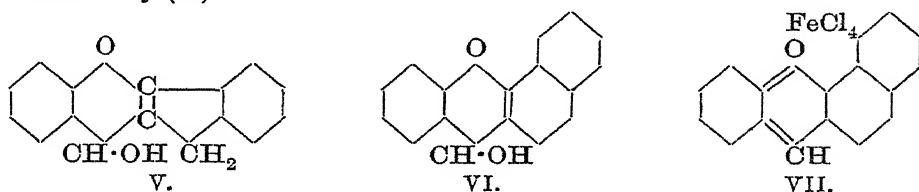
The platinichloride of the above pyranol was obtained in both

<sup>43</sup> S. von Kostanecki and V. Lampe, *Ber.*, 1908, **41**, 2373 ; *A.*, i, 671.

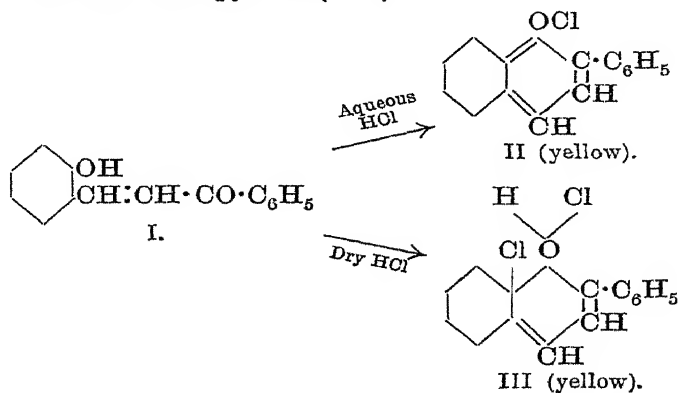
hydrated and anhydrous (III) forms, and all the ferrichlorides described were free from water.



Formula (IV), for example, represents the anhydroferrichloride of 2 : 3-indenobenzopyranol(1 : 4), the free base having the structure indicated by (V) :



The ortho-quinonoid formula is adopted for these salts because they are coloured, and in every way comparable with those of naphthaxanthhydrol. Formulæ (VI) and (VII) represent respectively this substance and its anhydroferrichloride. It will be seen that the heterocyclic nuclei of 2 : 3-indenobenzopyranol(1 : 4) and naphthaxanthhydrol are similarly constituted (V and VI), and their salts, for example, the anhydroferrichlorides (IV and VII), are formed in a similar manner with elimination of water. Now the naphthaxanthhydrol anhydroferrichloride must be formulated as an ortho-quinoid whether the double linkings are represented as in (VII) or whether they are turned towards the naphthalene nucleus. Accordingly, it may fairly be assumed that the same ortho-quinonoid structure exists in the salts of 2 : 3-indenobenzopyranol(1 : 4).

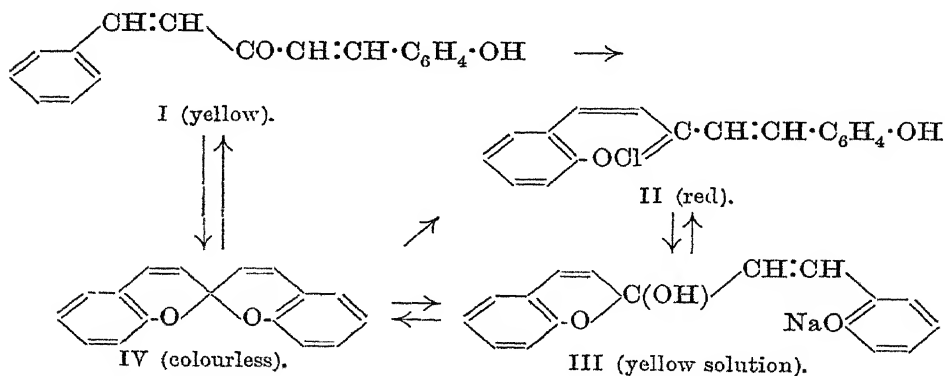


The action of hydrogen chloride on 2-hydroxybenzylideneacetophenone (I) under different conditions affords a noteworthy example of ring formation with production of oxonium salts. Hot concentrated hydrochloric acid acting on the ketone in glacial acetic acid produces 2-phenylbenzopyranol anhydrohydrochloride (II), a very soluble salt isolated in the form of its platinichloride,  $(C_{15}H_{11}OCl)_2PtCl_4$ .

Dry hydrogen chloride and the ketone interacting in ethereal solution give rise to the dichloride (III) (the hydrochloride of 2-phenylbenzopyranol anhydrohydrochloride).

The original memoir should be consulted for further examples of these interesting pyranol salts, and for a fuller exposition of the arguments adduced in favour of their constitutional formulæ.<sup>44</sup>

A closely allied series of oxonium salts has been produced from disalicylideneacetone (I); this substance when treated with alcoholic hydrochloric acid undergoes condensation to a red oxonium chloride (II), which furnishes a brick-red ferrichloride,  $C_{17}H_{13}O_2 \cdot FeCl_4$ . Dilute aqueous sodium hydroxide converts the 2-*o*-hydroxystyrylbenzopyrylium chloride (II) into the sodium salt, 2-*o*-hydroxystyrylbenzopyranol-2 (III), from which, however, the free carbinol could not be isolated, as dilute acids induce further condensation with the formation of a substance containing two heterocyclic nuclei. This so-called dibenzospiropyran (IV) is hydrolysed by strong acids to the oxonium salt, and by alcoholic soda to the original disalicylideneacetone (I).<sup>45</sup>



### *Indigotin and Indigoid Dyes.*

The investigations recently carried out on the dyes of the indigo group fall chiefly under four headings: (1) improvements in the phenylglycine synthesis of indigotin, (2) the production of halogenated

<sup>44</sup> W. H. Perkin, jun., R. Robinson, and M. R. Turner, *Trans.*, 1908, **93**, 1085.

<sup>45</sup> H. Decker and H. Felser, *Ber.*, 1908, **41**, 2997; *A.*, i, 906.

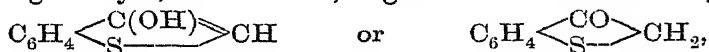
indigotins, (3) the synthesis of indigoid dyes containing sulphur, (4) the synthesis of more complex dyes, chiefly of the anthracene series, which are capable of employment in the hyposulphite vat.

1. Modifications in the process of synthesising indoxyl by heating phenylglycine with alkalis have formed the subject of many recent patents. The addition of magnesium powder to the fused mixture of phenylglycine with sodium and potassium hydroxides and barium oxide more than doubles the yield of indigotin subsequently precipitated by aerial oxidation from aqueous solutions of the melt. Fusion under greatly reduced pressure at 200—230° gives an 80 to 90 per cent. yield of indigotin.<sup>46</sup>

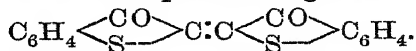
2. A well-defined chloroindigotin,  $C_{16}H_9O_2N_2Cl$ , has been prepared by direct chlorination of indigotin suspended in hot nitrobenzene. Bromination in the same medium has led to the formation of a tri- and two tetra-bromoindigotins, and more highly halogenated indigotins have been produced, containing both chlorine and bromine. The substitution of hydrogen by halogen in indigotin increases the brilliancy and fastness of the dye, and it is noteworthy that the leuco-derivatives of these halogenated indigotins differ from indigo-white in being coloured, the shade varying from yellow to brown.<sup>47</sup>

The sulphonic acids of the halogenated indigotins have also been prepared; their tinctorial properties differ considerably from those of indigo carmine.<sup>48</sup>

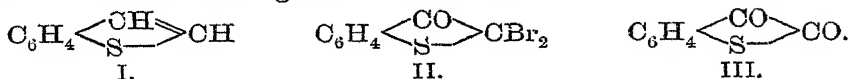
3. 2-Hydroxythionaphthen, an important compound in the synthesis of thioindigoid dyes, is obtained, together with its carboxylic acid,



by condensing chloroacetic and thiosalicylic acids or their esters in alkaline solutions and then heating the intermediate product, carb-methoxy-*o*-thiobenzoic acid,  $CO_2H \cdot C_6H_4 \cdot S \cdot CH_2 \cdot CO_2H$ , with sodium hydroxide at 180°. Oxidation of 2-hydroxythionaphthen, or its carboxylic acid, results in the formation of a red colouring matter, thioindigotin or 2:2'-bisthionaphthenindigotin,<sup>49</sup>



Thionaphthen (I), the parent substance of this group of dyes, is now readily obtained by reducing the synthetical 2-hydroxythionaphthen with zinc and glacial acetic acid:



<sup>46</sup> L. Lilienfeld, D.R.-P. 189021, 195352; *A.*, i, 371, 797.

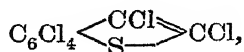
<sup>47</sup> D.R.-P. 193438, 193970, 193971, 195085, 195291; *A.*, i, 468, 695, 798.

<sup>48</sup> C. G. Schwalbe and H. Jochheim, *Ber.*, 1908, 41, 3798; *A.*, i, 1019.

<sup>49</sup> D.R.-P. 192075, 194237, 194254; *A.*, i, 451, 672.

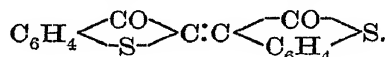
2-Hydroxythionaphthen yields 1:1-dibromo-2-ketodihydrothionaphthen (II), and this, on treatment with lead acetate, gives rise to the intensely yellow thionaphthenquinone (III). Like hydroxythionaphthen, the dibromide and the quinone are employed in the synthesis of thioindigoid dyes.<sup>50</sup>

The interaction of thionyl chloride, and various styrene derivatives, at 180—270°, leads to the formation of thionaphthen compounds,  $\alpha\beta$ -dibromostyrene giving rise to hexachlorothionaphthen,

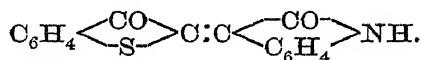


a substance containing only carbon, chlorine, and sulphur.<sup>51</sup>

The condensation of 2-hydroxynaphthen and thionaphthenquinone furnishes thioindirubin, 2:3-bisthionaphthenindigotin,<sup>52</sup>

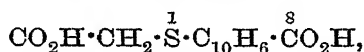


Dyes containing indigotin and thionaphthen nuclei have been synthesised. Isatin and hydroxythionaphthen give rise to thioindigo-scarlet, 2-thionaphthen-3-indole-indigotin,



The isomerides, 2-thionaphthen-2-indole-indigotin and 3-thionaphthen-2-indole-indigotin, are obtained from indoxyl with thionaphthen dibromide and thionaphthenquinone respectively.

The application of *peri*-carboxymethylthionaphthoic acid,



in the preparation of blue thioindigoid dyes has been patented.<sup>53</sup>

4. Certain complex anthracene derivatives containing nitrogen have the property of yielding colouring matters suitable for the hyposulphite dye vat.<sup>54</sup>

Flavanthren, which possesses this property, may be conveniently considered at this stage. This yellow colouring matter is remarkable because it yields a series of reduction products, most of which are more intensely coloured than the original substance. The progressive reduction of flavanthren indicates the formation of seven reduction products, five of which have actually been isolated.

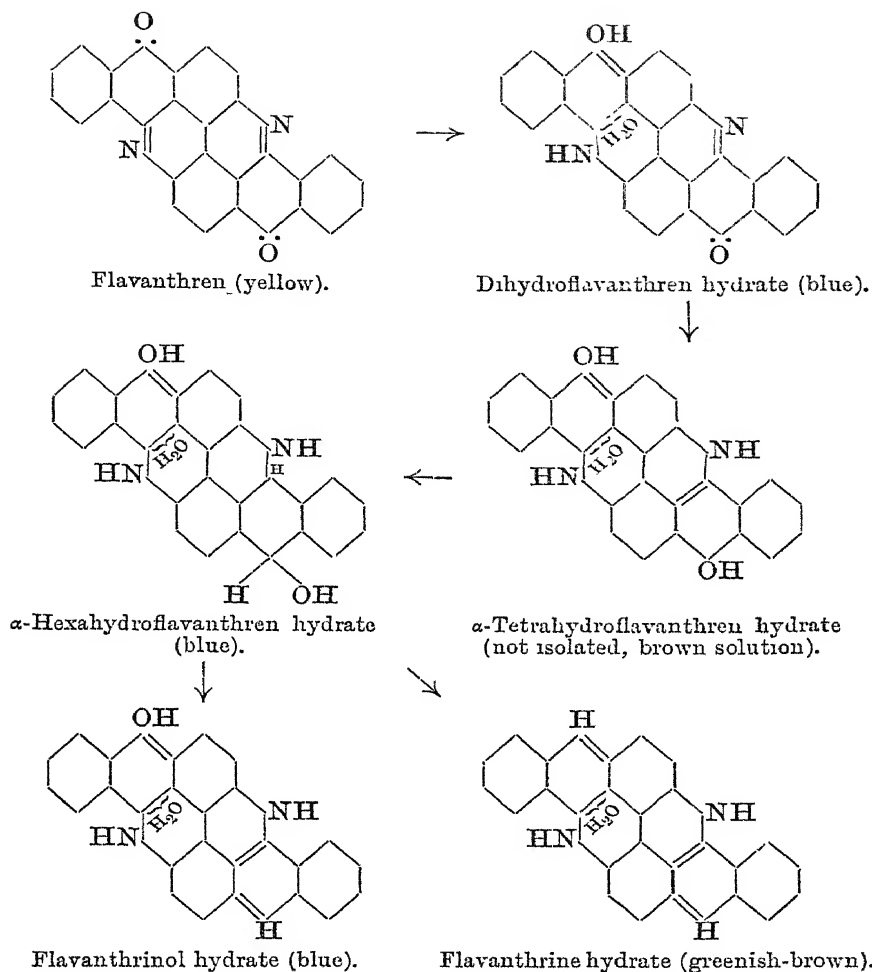
<sup>50</sup> A. Pezdzik, P. Friedländer, and P. Koeniger, *Ber.*, 1908, **41**, 227; *A.*, i, 200.

<sup>51</sup> G. Barger and A. J. Ewins, *Trans.*, 1908, **93**, 2086.

<sup>52</sup> P. Friedlander, *Monatsh.*, 1908, **29**, 359, 375; *A.*, i, 673.

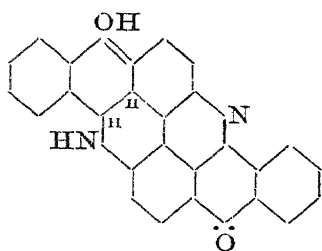
<sup>53</sup> D.R.-P. 198050; *A.*, i, 797.

<sup>54</sup> D.R.-P. 197554; *A.*, i, 807.

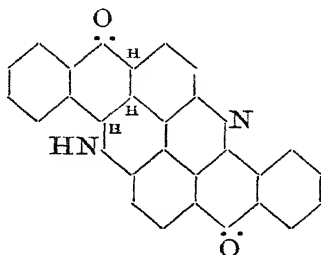
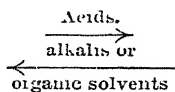


The foregoing diagram represents, according to Scholl, the successive stages in the reduction of flavanthren. The products thus isolated contain water of hydration, which is assumed to be attached to two carbons united by a double linking in one of heterocyclic rings. Dihydroflavanthren (green),  $\alpha$ -hexahydroflavanthren (blue), flavanthrinol (blue), and flavanthrine (brown) have, however, all been obtained in the anhydrous condition by expelling the water at 150—200°. This dehydration is not accompanied by any marked change in colour. The di-,  $\alpha$ -tetra-, and  $\alpha$ -hexa-hydroflavanthren hydrates are obtained by alkaline reducing agents, flavanthrinol is formed by heating  $\alpha$ -hexahydroflavanthren hydrate, and flavanthrine hydrate is produced by reducing flavanthren or the foregoing hexahydro-hydrate

with red phosphorus and hydriodic acid at  $210^{\circ}$ . At  $170^{\circ}$ , flavanthren, when reduced, gives rise to another tetrahydroflavanthren, to which in solution the following constitution (I) is ascribed, although when precipitated it probably exists in the ketonic form (II). This  $\beta$ -tetrahydroflavanthren cannot be hydrated, for it already contains two hydrogen atoms in the position occupied by water in the other reduction products.



I.  $\beta$ -Tetrahydroflavanthren  
red in solution (enol).



II. Green precipitated ketonic  
form.

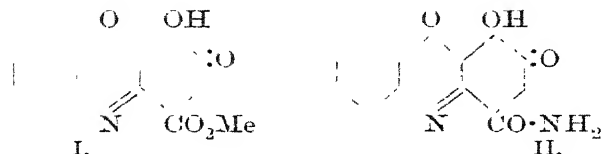
This production of intensely coloured reduction products from a faintly coloured substance is a striking example of the rule that the partial conversion of the chromophores of a colouring matter into auxochromic groups brings about an intensification of the colour. The partial reduction of yellow picric acid to dark brown picramic acid is a case in point. This generalisation accounts for the colour of the intermediate reduction products of flavanthren. The colour of the final product, flavanthrine, like that of meso- and  $\beta$ -anthramines, may be referred to the fact that they are all derivatives of anthracene, a hydrocarbon which must be regarded as having a chromophoric ortho-quinonoid constitution.<sup>55</sup>

#### *Oxazine Group.*

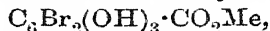
The oxazine dye produced by the condensation of nitrosodimethylaniline and methyl gallate is termed "prune" (I), and an interesting series of derivatives may be obtained from it by the action of aniline and similar aromatic amines. Pruneanilide was formerly supposed to be an additive compound of the oxazine and aniline, but it has now been shown to be a substituted derivative, the dye and aniline condensing in molecular proportions while the hydrogen which should be displaced is employed in reducing another molecule of prune to its leuco-derivative. Actually, the yield of pruneanilide was doubled by blowing air through the mixture. A similar result was obtained with coelestin blue B [the oxazine (II) from nitrosodimethylaniline and gallamide],

<sup>55</sup> R. Scholl, *Ber.*, 1908, 41, 2304, 2534; *A.*, i, 696, 740.

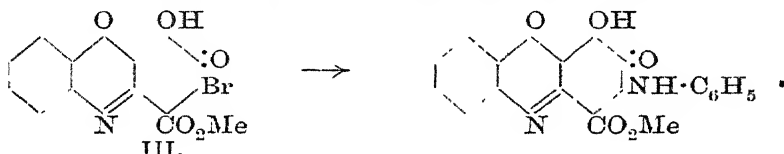
the yield of anilide being considerably increased by the introduction of air.



The constitution of pruneanilide has been demonstrated by condensing nitrosodimethylaniline and methyl dibromogallate,

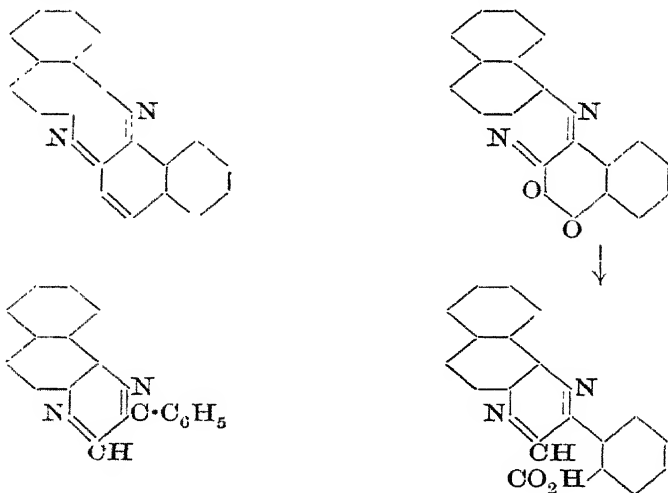


when bromoprune is produced, which must have the following constitution (III). When this bromoprune is heated with an alcoholic solution of aniline, pruneanilide results. Accordingly the anilino-residue occupies the position adjacent to the quinonic oxygen (IV). The anilide of coelestin blue B has a similar constitution.<sup>56</sup>



### The Azine Group.

The relationship between azines and quinoxalines ("ethopyrazines") is well illustrated by the conversion of the two isomeric  $\alpha\beta$ -dinaphthazines into bases of the quinoxaline series. *s*- $\alpha\beta$ -Dinaphthazine is first

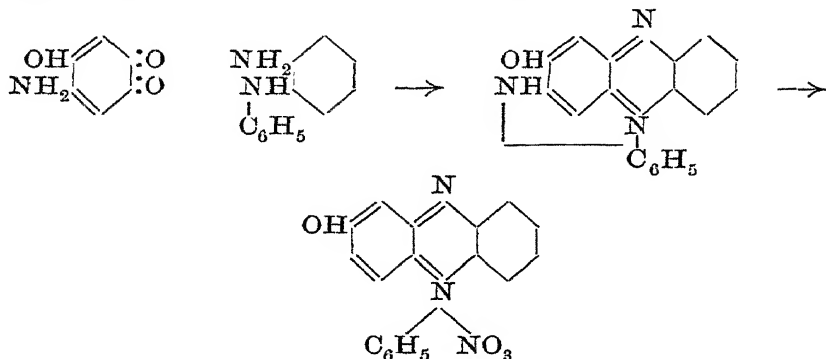


<sup>56</sup> E. Grandmougin and E. Bodmer, *Ber.*, 1908, 41, 604; *A.*, i, 289, REP.—VOL. V. M

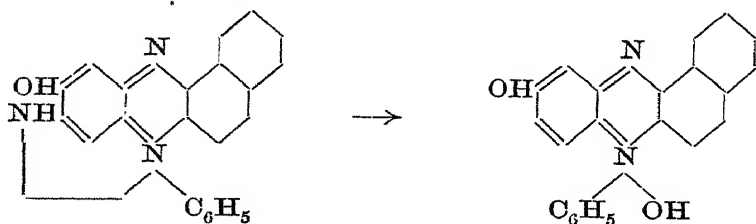


oxidised by chromium trioxide into diketo-*s-αβ*-dinaphthazine. This substance, when heated with concentrated sodium hydroxide, gives rise to 2-phenylnaphthaquinoxalinecarboxylic acid, which, on heating, loses carbon dioxide, and yields 2-phenylnaphthaquinoxaline ("2-phenylnaphthapyrazine"). *as-αβ*-Dinaphthazine is converted into 3-phenylnaphthaquinoxaline by a precisely similar series of changes.<sup>57</sup>

The prasindones are a group of hydroxyazonium bases containing a hydroxyl group in the para-position with respect to the azonium nitrogen. In some cases, water is eliminated from the azonium and phenolic hydroxyls, so that the base exists in the form of an anhydride. An attempt to prepare the simplest member of this series has not been successful. *o*-Aminodiphenylamine has been condensed with 3-amino-4-hydroxy-*o*-benzoquinone, and the following series of changes has been realised, but it was not found possible to isolate the base corresponding with the final product: the prasindone nitrate.



When 2-anilino-1-aminonaphthalene was substituted for *o*-aminodiphenylamine in the foregoing condensation, the synthesis was carried a stage further, but in this case the prasindone hydrate, although actually isolated, could not be dehydrated.<sup>58</sup>

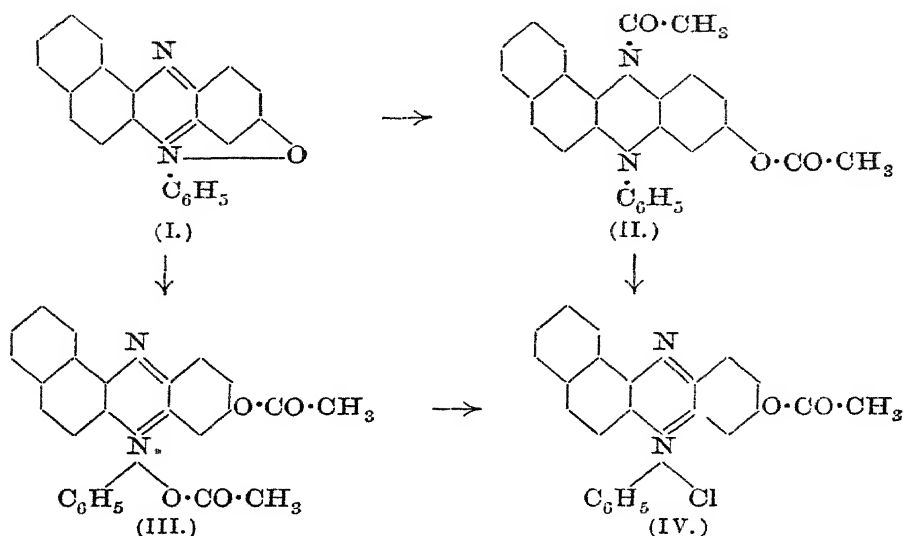


Further evidence in favour of Kehrman's betaine formula for isorosindone (I) has been obtained by converting it into the chloride of

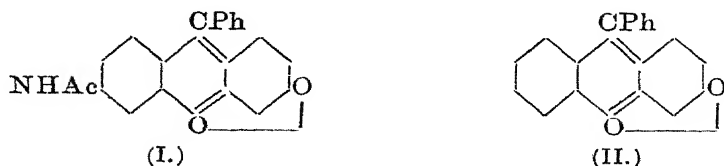
<sup>57</sup> O. Fischer and E. Schindler, *Ber.*, 1908, **41**, 390; *A.*, i, 221.

<sup>58</sup> F. Kehrman and R. Schwarzenbach, *ibid.*, 472; *A.*, i, 297.

its acetyl derivative (IV) by two distinct processes. In one the compound is simultaneously reduced and acetylated by zinc dust and acetic anhydride, the product, a diacetyl leuco-derivative (II), being then oxidised to the chloride. In the other process the isorosindone is treated with acetic anhydride alone, when the acetate (III) of its acetyl derivative is directly produced, and can be converted into the corresponding chloride.<sup>59</sup>



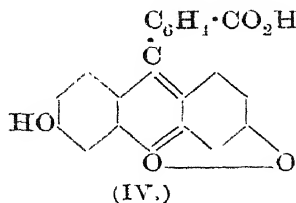
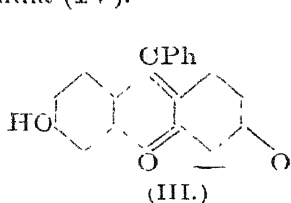
Carboxonium dyes with a structure somewhat similar to the preceding substances have quite recently been obtained by condensing *m*-acetylaminophenol and benzotrichloride in nitrobenzene at 16°. One of these is acetylaminophenylfluorone (I), to which an ortho-quinonoid structure is ascribed. The non-acetylated base is of great



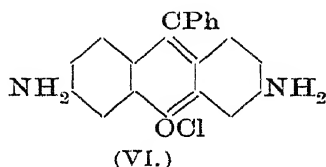
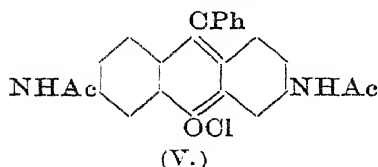
interest, as on eliminating the amino-group, phenylfluorone (II) is obtained, which is the chromogen of fluorescein. Hydroxyphenylfluorone (III), produced by replacing the amino-group by hydroxyl, is identical with resorcinolbenzein, and is remarkably like fluorescein, which, as its

<sup>59</sup> F. Kehrman and K. L. Stern, *Ber.*, 1908, 41, 12; *A.*, i, 220.

carboxylic acid, should, if Kehrman's formulation be accepted, have the formula (IV).

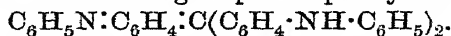


The other condensation product is diacetylaminophenorosamine chloride (V), which yields an unstable colour base changing rapidly into a colourless, stable form. Hydrolysis leads to the simplest rosamine, the salt of which is represented by (VI).<sup>60</sup>



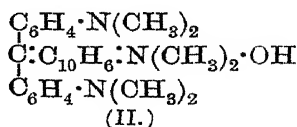
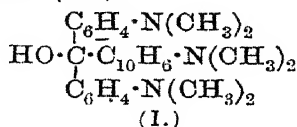
### *The Rosaniline Group.*

The researches of Baeyer and Villiger have shown that many bases of the triphenylmethane group exist in two forms, one colourless and the other coloured. There is little doubt that the colourless bases have the carbinol formula,  $\text{HO}\cdot\text{C}(\text{C}_6\text{H}_4\text{NR}_2)_3$ , but some uncertainty still exists as to the nature of the coloured amines. In many cases the coloured amine is the dehydrated imino-base, which has only been obtained pure when the amino-groups are phenylated, as in

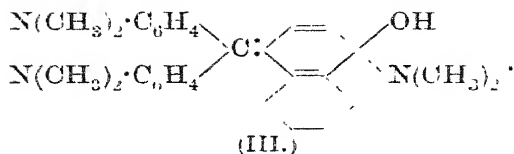


The methylated rosanilines have as yet only been isolated in the colourless carbinol form, and although the observations of Hantzsch and Osswald indicate that isomeric quinoneimmonium bases of this series may exist, these substances have not been obtained in a state of purity.

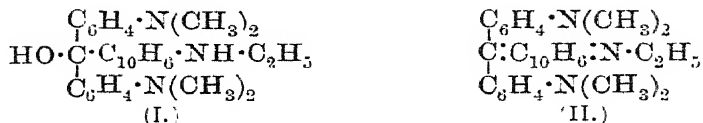
Naphtho-blue,  $\text{NMe}_2\text{Cl}:\text{C}_{10}\text{H}_6:\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ , has yielded its base in two isomeric forms, the colourless carbinol (I) (m. p.  $155^\circ$ ) and the dark green, quaternary ammonium hydroxide (II) (m. p.  $261^\circ$ ), which may possibly have the alternative pseudo-ammonium formula (III).



<sup>60</sup> F. Kehrman and O. Dengler, *Ber.*, 1908, 41, 3440; *A.*, i, 1002.



Victoria-blue R,  $\text{NH}_4\text{EtCl} \cdot \text{C}_{10}\text{H}_6 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , has also given rise to a coloured as well as a colourless base, but these substances are not isomeric. The colourless compound is the carbinol (I) (m. p.  $170^\circ$ ), but the coloured substance is the anhydrous imino-base (II) (m. p.  $192^\circ$ ).



The composition of these two pairs of diphenylnaphthylmethane bases has been confirmed in each case by complete analyses,<sup>61</sup> which show that the substances were obtained in a fairly pure state.

The corresponding diphenylnaphthylmethane colouring matter, containing methyl instead of ethyl in the foregoing formulæ, gives rise also to the corresponding colourless carbinol and the coloured imino-base.

All attempts to isolate the quinonoid form of the bases from crystal-violet, malachite green, and *o*-chloromalachite green were unsuccessful; although the coloured bases could be seen in solution, they were too unstable to be analysed.<sup>62</sup>

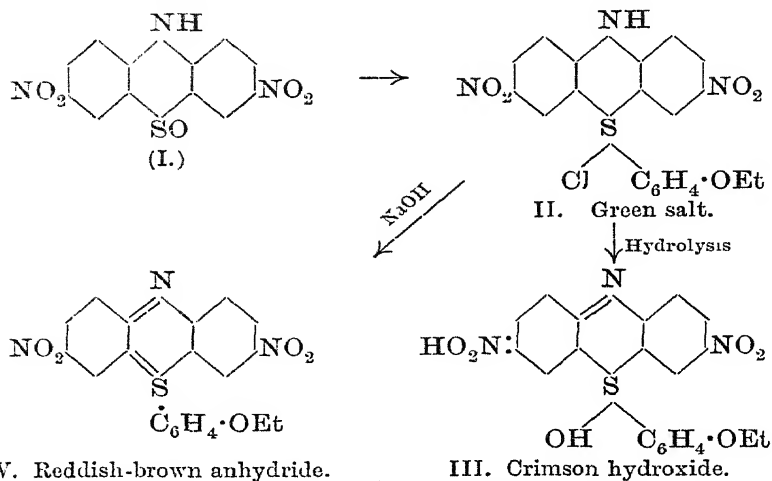
### *Cyclic Sulphur Compounds.*

One of the nitration products of thiodiphenylamine is the dinitro-sulphoxide (I), which has been taken as the starting point in the synthesis of *S*-phenylphenazothionium hydroxide and its salts. When condensed with phenol or phenetole in concentrated sulphuric acid, the sulphoxide gives rise to the sulphate of a phenazothionium base, the chloride of which is represented by formula (II).

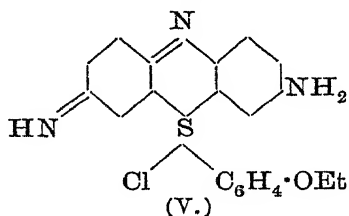
*S*-Phenetyl-3 : 3'-dinitrophenazothionium chloride undergoes hydrolysis to the base *S*-phenetyl-3 : 3'-dinitrophenazothionium hydroxide (III), but when treated with aqueous alkali hydroxide the anhydride (IV) (anhydro-*S*-phenetyl-3 : 3'-dinitrophenazothionium) is set free.

<sup>61</sup> E. Noelting and K. Philipp, *Ber.*, 1908, **41**, 579 : *A.*, i, 295.

<sup>62</sup> *Ibid.*, 3908 ; *A.*, 1909, i, 61.

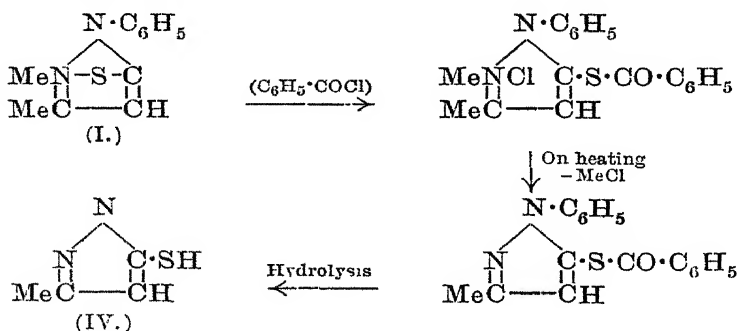


The chloride (II) has been reduced to a diamine, which, on oxidation, gives rise to *S*-phenetyl-3:3'-diaminophenazothionium chloride (V).



Corresponding phenazothionium salts have been produced containing hydroxyphenyl in the place of phenetyl.<sup>63</sup>

Thiopyrine, the sulphur analogue of antipyrine, is regarded by Michaelis as having the formula (I). It has now for the first time been converted into 1-phenyl-3-methyl-5-thiopyrazolone (IV) in the manner indicated in the following diagram :

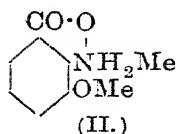
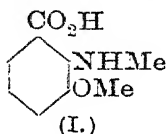


<sup>63</sup> S. Smiles and T. P. Hilditch, *Trans.*, 1908, **93**, 145, 1687.

The presence of the thiol group SH is indicated by the mode in which the thiopyrazolone undergoes oxidation. Alkaline hydrogen peroxide gives rise to the sulphonic acid, whilst nitrous acid or iodine in potassium iodide solution leads to the disulphide. Nevertheless, 1-phenyl-3-methyl-5-thiopyrazolone also reacts in its thiocarboxyl form, and, like phenylmethylpyrazolone, it condenses with aldehydes and ketones.<sup>64</sup>

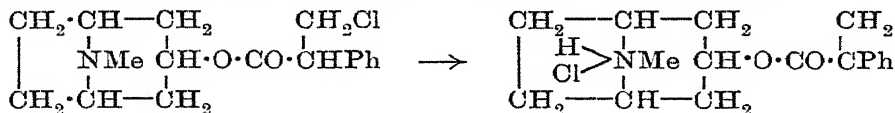
### Alkaloids.

Damascenine, the alkaloid from *Nigella*, has been investigated, and its constitution established. Boiling with alkalis converts it into an isomeride, damascenic acid, which by a series of steps yields 2-amino-3-hydroxybenzoic acid, proving it to be 2-methylamino-3-methoxybenzoic acid (I). The alkaloid, being devoid of acid properties, appears to be a betaine (II).



Methyldamascenine, present in the same plant, proves to be the methyl ester of damascenic acid. An attempt to synthesise the alkaloid, starting from methylanthranilic acid, failed owing to the impossibility of introducing methoxyl or hydroxyl in place of the amino-group in position 3, the diazonium compound changing into a stable azimino-compound.<sup>65</sup>

Atropine may be synthesised by a method giving a much better yield than does the condensation of tropine with tropic acid, by acetylation of tropic acid, conversion into the chloride, condensation with tropine hydrochloride, and elimination of the acetyl group, the last process taking place spontaneously when the acetyltropine is allowed to remain a short time in aqueous solution. On the other hand, when an attempt is made to replace the chlorine in  $\beta$ -chlorohydratropyltropine by hydroxyl, an intramolecular change takes place, hydrogen chloride being transferred, and *apoeatropine* hydrochloride is obtained :



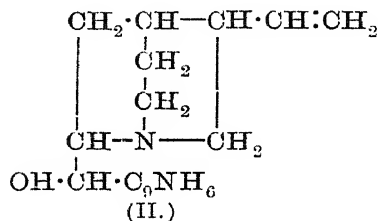
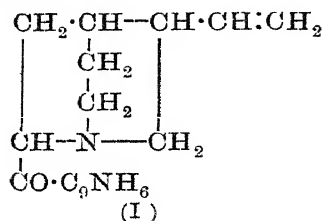
This *apoeatropine* synthesis is a general one for tropeines, starting from  $\alpha$ -,  $\beta$ -, or  $\gamma$ -halogenated propionic or *n*-butyric acids.<sup>66</sup>

<sup>64</sup> A. Michaelis, *Annalen*, 1908, **361**, 251; *A.*, i, 688.

<sup>65</sup> O. Keller, *Arch. Pharm.*, 1908, **246**, 1; *A.*, i, 283.

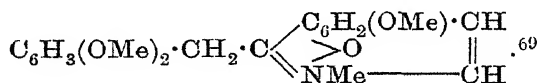
<sup>66</sup> R. Wolfenstein and L. Mamlock, *Ber.*, 1908, **41**, 723; R. Wolfenstein and J. Rolle, *ibid.*, 733; *A.*, i, 281, 282.

A contribution to the study of cinchonine has been made in the form of an examination of cinchoninone, the ketone obtained by oxidation of the alkaloid. This ketone is amphoteric, and also exhibits enol-keto-tautomerism, yielding both an oxime and an *O*-benzoyl derivative. By the action of nitrous acid, cinchonic acid and an oxime are obtained, the latter yielding Koenig's *meroquinene* on hydrolysis. This leads to formulæ (I and II) for cinchoninone and cinchonine respectively :<sup>67</sup>



Although little progress has been made towards establishing the constitution of the strychnos alkaloids, nevertheless crystalline acids have now been obtained by oxidation, the composition of which indicates that both alkaloids contain a secondary alcohol grouping.<sup>68</sup>

When papaverinium alkyl salts are treated with very dilute alkalis, the liberated papaverinium hydroxides undergo condensation to phenolbetaines. Thus *N*-methylpapaverinium methosulphate yields the phenolbetaine,



In the morphine group of alkaloids, a synthesis of a compound obtained in the partial breaking down of morphine has been effected for the first time. Morpholquinone is known to be 3:4-dihydroxy-phenanthraquinone, and this may be prepared from 3-nitrophenanthraquinone by reduction, diazotisation, and conversion into the 3-hydroxy-compound, nitration in the 4-position, a repetition of the reduction and diazotisation giving morpholquinone.<sup>70</sup>

$\psi$ -apocodeine is the 3-methyl ether of *apomorphine*, and thus stands in the same relation to *apomorphine* as codeine does to morphine.<sup>71</sup>

Much work has also been carried out on the constitution of

<sup>67</sup> P. Rabe, *Ber.*, 1908, **41**, 62; *A.*, **1**, 100.

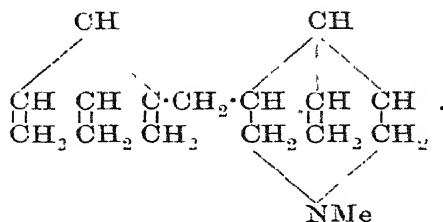
<sup>68</sup> H. Leuchs, *ibid.*, 1711; *A.*, **1**, 563.

<sup>69</sup> H. Decker and G. Dunant, *Annalen*, 1908, **358**, 288; *A.*, **1**, 204.

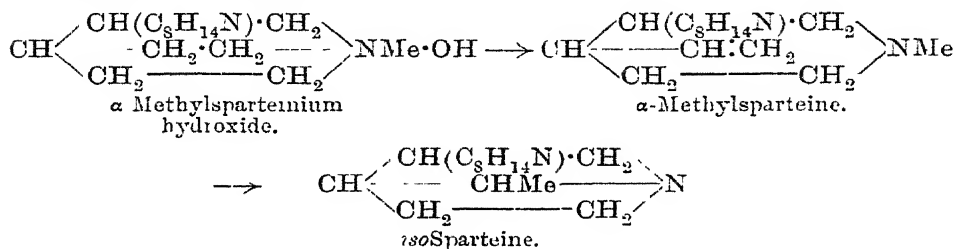
<sup>70</sup> J. Schmidt and J. Soll, *Ber.*, 1908, **41**, 3696; *A.*, **1**, 995.

<sup>71</sup> L. Knorr and F. Raabe, *ibid.*, 3050; *A.*, **1**, 908.

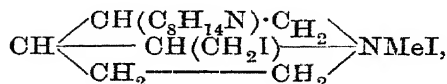
sparteine<sup>72</sup> by means of a study of the reactions of  $\alpha$ -methylsparteine. When degraded by Hofmann's reaction, methylsparteine yields methylhemisparteilene,



The methylsparteines behave as unsaturated bases, having a methyl group attached to nitrogen. The *isosparteine* into which they may be converted is a ditertiary base, which does not reduce acid permanganate. The conversion may be carried out by heating  $\alpha$ -methylsparteine di-iodide with water at 125°, when isomeric change to *isosparteine* methiodide takes place.



The reverse change may be carried out by heating  $\alpha$ -methyl*isosparteinium* hydroxide in a vacuum, when it gives  $\alpha$ -methylsparteine. The latter compound takes up two atoms of iodine to form the methiodide of an iodo-base, which behaves as if it were an iodo*isosparteine*,



but it is possible that its formation is due to the isomerisation of the  $\alpha$ -methylsparteine under the influence of hydrogen iodide.

Jateorrhizine and columbamine, alkaloids from columba root, have been further investigated,<sup>73</sup> and the monomethyl ether of columbamine is found to be identical with the dimethyl ether of jateorrhizine. The acid obtained on oxidation of this ether is a trimethoxy-o-

<sup>72</sup> C. Moureu and A. Valeur, *Compt. rend.*, 1907, **145**, 815, 929, 1184, 1343; 1908, **146**, 79; **147**, 127; *Bull. Soc. chim.*, 1908, [iv], **3**, 674; *A.*, i, 43, 44, 103, 206, 563, 736, 1006.

<sup>73</sup> K. Feist, *Arch. Pharm.*, 1907, **245**, 586; *A.*, i, 100.



phthalic acid, but it has not yet been determined whether the methoxyl groups have the 3:4:5- or 3:4:6-position. A third alkaloid, palmatine, closely resembling berberine, is also present in the root, but its relation to the other two is unknown.

### *Polypeptides.*

The progress in the building up of polypeptide molecules has been exceedingly rapid during the past year. Perhaps the most important step that has been made is that of introducing tyrosine groups into the molecule. The tyrosine group is of such frequent occurrence in natural proteins that this advance was necessary before compounds showing the reactions of the true proteins could be prepared, especially as the difference between the naturally occurring and the synthetic polypeptides is now recognised as consisting less in the number of amino-acid groups present than in the conjunction, in natural substances, of groups of several different kinds.

The usual method of synthesis is not applicable when an amino-hydroxy-acid, such as tyrosine, is employed, because of the action of phosphorus pentachloride on the hydroxyl group. This may be protected by the introduction of the carbomethoxyl group, which resists the action of phosphorus pentachloride and acyl chlorides, and is readily removed afterwards by hydrolysis. The protecting group is introduced by means of methyl chlorocarbonate. The products are, however, inactive.<sup>74</sup>

A tetrapeptide was isolated last year from silk, and was shown to consist of two glycine groups and one group each of *d*-alanine and *l*-tyrosine. Several attempts to synthesise this substance have been made, but in every case the product was found to differ from the natural polypeptide in not being precipitated by ammonium sulphate, or in only being precipitated from very concentrated solutions. Such compounds, isomeric with the tetrapeptide sought after, have been prepared by the action of *l*-tyrosine ester on chloroacetyl-*d*-alanyl-glycine, and by coupling glycine-*d*-alanine anhydride with chloroacetyltyrosyl chloride methyl carbonate, followed by hydrolysis. The glycylytyrosylglycyl-*d*-alanine obtained in the second case is probably a mixture of stereoisomerides.<sup>75</sup> Various tyrosine polypeptides, derived from glycine, *d*-alanine, and *l*-leucine, were also not precipitated by ammonium sulphate.<sup>76</sup>

The 3:5-di-iodo-*l*-tyrosine group has also been introduced, on account of its occurrence in the proteins of coral. Glycyldi-iodotyro-

<sup>74</sup> E. Fischer, *Sitzungsber. K. Akad. Wiss. Berlin*, 1908, 542, *A.*, i, 544.

<sup>75</sup> E. Fischer, *Ber.*, 1908, 41, 850, 2860; *A.*, i, 324, 887.

<sup>76</sup> E. Abderhalden and A. Hirszowski, *ibid.*, 2840; *A.*, i, 887.

sine has been synthesised,<sup>77</sup> starting from the action of iodine on tyrosine.

Various dipeptides have been prepared containing the *d*-valine group, which are of interest, not only in connexion with polypeptide synthesis, but also for the study of the Walden inversion.<sup>78</sup> More complex groups have also been introduced, notably the  $\alpha$ -aminostearyl group<sup>79</sup> and  $\beta$ -amino-acid residues, such as those of  $\beta$ -aminobutyric acid and  $\alpha$  methylisoserine.<sup>80</sup>

It is found that glycine ethyl ester, like ethyl oxalate, may be reduced with sodium amalgam, the final product, after treatment with alcoholic hydrogen chloride, being aminoacetal.<sup>81</sup> The application of a similar method of reduction to polypeptides gives unsatisfactory yields, but the corresponding aminoacetals are readily prepared by the condensation of aminoacetal with chloroacyl chlorides and treatment of the products with ammonia.

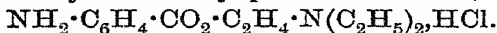
The presence of histidine in many natural proteins, and the existence of proline (pyrrolidine-2-carboxylic acid) in the products of the hydrolysis of gelatin, have led Fischer and his pupils to include these groups also in the synthetic scheme, and methods of synthesis have therefore been devised for the purpose of preparing the materials.<sup>82</sup>

*l*-Leucyl-*l*-histidine is stable towards concentrated hydrochloric acid, and since both *l*-leucine and *l*-histidine are present in oxyhæmoglobin, the dipeptide was sought for, but unsuccessfully, in the products of hydrolysis of that substance.

The use of hydrofluoric acid has been recommended for the hydrolysis of proteins, as causing less secondary reactions than any other acid.<sup>83</sup>

### *Synthetical Therapeutic Agents.*

Considerable activity is being shown in the production of local anæsthetics of the "novocaine" type. This substance itself is the hydrochloride of diethylaminoethyl *p*-aminobenzoate,



A series of similarly constituted compounds has been prepared, and their physiological action has been ascertained. Some of these substances have pronounced local anæsthetic properties, but are not

<sup>77</sup> E. Abderhalden and M. Guggenheim, *Ber.*, 1908, **41**, 1237; *A.*, i, 420.

<sup>78</sup> E. Fischer and H. Scheibler, *Annalen*, 1908, **363**, 136; *A.*, i, 957.

<sup>79</sup> E. Fischer and W. Kropp, *ibid.*, **362**, 338; *A.*, i, 773.

<sup>80</sup> F. W. Kay, *ibid.*, 348; *A.*, i, 773.

<sup>81</sup> E. Fischer, *Ber.*, 1908, **41**, 1019; *A.*, i, 323.

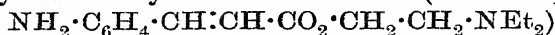
<sup>82</sup> E. Fischer and A. Kramer, *ibid.*, 2728; E. Fischer and L. H. Cone, *Annalen*, 1908, **363**, 107; E. Fischer and G. Reif, *ibid.*, 118; *A.*, i, 858, 1004, 1007.

<sup>83</sup> L. Hugouneq and A. Morel, *Compt. rend.*, 1908, **146**, 1291; *A.*, i, 706.

suitable for use in medicine, owing either to their high general toxicity or to the local irritation produced by their injection.<sup>84</sup>

In view of these results, it is open to doubt whether the many compounds recently described in patents are, in general, of much therapeutic value.

The hydrochlorides of the dialkylaminoalkyl benzoates, such as  $C_6H_4 \cdot CO_2 \cdot CH_2 \cdot CH_2 \cdot NEt_3 \cdot HCl$ , are stated to be useful anæsthetics,<sup>85</sup> whilst the alkylaminoalkyl aminocinnamates (for example,

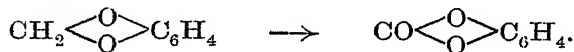


are said to surpass the alkylaminoalkyl benzoates in this respect.<sup>86</sup>

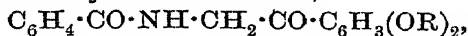
It is claimed that the alkylaminoalkyl salicylates unite these anæsthetic properties with those of salicylic acid.<sup>87</sup>

Salicylic acid and its acetyl derivative ("aspirin") have certain undesirable physiological properties, which are said to be favourably modified in the recently-described anhydrides of acylsalicylic acids. Of these products, acetylsalicylic anhydride,  $O(CO \cdot C_6H_4 \cdot O \cdot CO \cdot CH_3)_2$ , and cinnamoylsalicylic anhydride,  $O(CO \cdot C_6H_4 \cdot O \cdot CO \cdot CH : CH \cdot C_6H_5)_2$ , appear to be the most promising.<sup>88</sup>

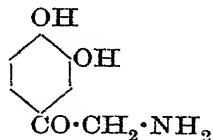
The recent commercially successful synthesis of the powerful hæmostatic adrenaline by the Farbwerke vorm. Meister, Lucius, and Brüning has stimulated research in this direction. An interesting series of observations on the conversion of catechol methylene ethers into cyclic carbonates by the action of thionyl chloride may be mentioned at this stage.<sup>89</sup>



The benzoylaminoacetylcatechol ethers,



when hydrolysed with aqueous acids under pressure, yield amino-



acetylcatechol, which is stated to have powerful hæmostatic properties like the active principles of the suprarenal capsules.<sup>90</sup>

The root of Canadian hemp (*Apocynum cannabinum*) retards the heart in systole. Apocynin, one of its physiologically active con-

<sup>84</sup> F. L. Pym, *Trans.*, 1908, **93**, 1793.

<sup>85</sup> D.R.-P. 187209; *A.*, i, 167.

<sup>86</sup> D.R.-P. 187593; *A.*, i, 169.

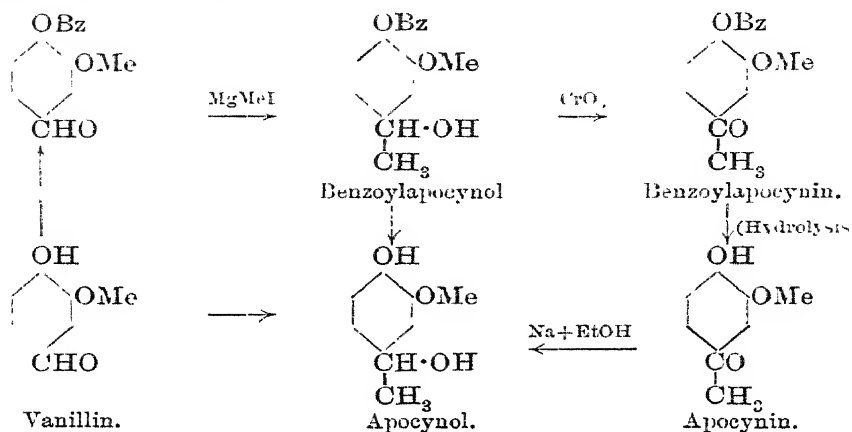
<sup>87</sup> D.R.-P. 188571; *A.*, i, 176.

<sup>88</sup> D.R.-P. 201325 and 201326; *A.*, i, 984.

<sup>89</sup> G. Barger and A. J. Ewins, *Trans.*, 1908, **93**, 563, 735, 2081.

<sup>90</sup> D.R.-P. 189483; *A.*, i, 262.

stituents, has been examined, and shown to be identical with aceto-vanillone. This conclusion has been confirmed by the synthesis of apocynin from vanillin.<sup>91</sup>



5:5-Diethylbarbituric acid ("veronal") and its homologues still receive much attention, and new methods of preparation form the subjects of many patents. Practically quantitative yields of these acids may be obtained by treating with nitrous acid the dialkylmalonylguanidines produced by condensing ethyl dialkylmalonates with guanidine.<sup>92</sup> A detailed study of the dialkylmalonic acids has brought to light the interesting fact that complex anhydrides of these substances may be produced by treating the acid chlorides with aqueous pyridine. The duodecimolecular anhydride of diethylmalonic acid has in ethylene dibromide or benzene a complexity corresponding with the formula  $\left[ \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{smallmatrix} \right] > \text{C} < \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} > \text{O} \Big]_{12}$ . In nitrobenzene the degree of association is diminished to that of an octamolecular anhydride.<sup>93</sup>

### Organic Derivatives of Arsenic.

The last few years have witnessed a great revival of interest in the study of organic derivatives of arsenic, owing to the circumstance that certain of these substances have proved efficacious in the therapeutics of diseases of protozoic origin.

Sodium *p*-aminophenylarsonate ("atoxyl") and its acetyl derivative have been successfully employed in the treatment of trypanosomiasis (sleeping sickness). The former of these substances was discovered by

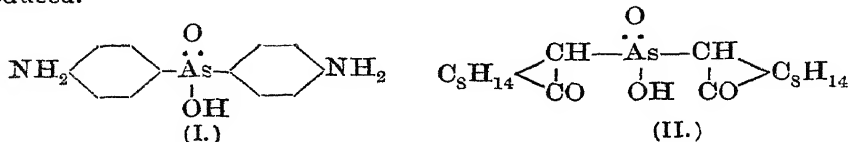
<sup>91</sup> H. Finnemore, *Trans.*, 1908, **93**, 1513, 1520.

<sup>92</sup> D.R.-P. 189076; *A.*, i, 370.

<sup>93</sup> A. Einhorn, *Annalen*, 1908, **359**, 145; *A.*, i, 312.

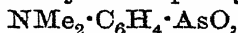
Béchamp in 1863, but its true nature was discovered only in 1907 by Ehrlich and Berthelm.

*p*-Aminophenylarsonic acid,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}(\text{OH})_2$ , is the chief product of the interaction of aniline and aniline arsenate at  $180^\circ$ , but Pyman and Reynolds have recently demonstrated that a small amount (2 or 3 per cent.) of bis-*p*-aminophenylarsinic acid (I) is simultaneously produced.<sup>94</sup>



These investigators have also prepared the corresponding bis-2-aminotolyl-5-arsinic acid, so that the reaction is probably a general one. These compounds are the aromatic analogues of cacodylic acid,  $\text{AsMe}_2\text{O} \cdot \text{OH}$ . The camphor analogue, dicamphorylarsonic acid (II), has recently been isolated from the products of the action of arsenious chloride on sodium camphor.<sup>95</sup>

The use of arsenious chloride for the introduction of arsenic into aromatic compounds was first studied by Michaelis and his collaborators. The dimethylaminophenylarsine oxide,



obtained from the chloride and dimethylaniline, has now been oxidised to dimethyl-*p*-aminophenylarsonic acid (dimethylatoxyl) by alkaline hydrogen peroxide.<sup>96</sup>

Aminoarsonic acids can be obtained from all primary aromatic amines having an unsubstituted para-position, and by means of the diazo-reaction the corresponding hydroxy-arsonic acids have been prepared.<sup>97</sup>

Phenylarsonic acid gives a nitrophenylarsonic acid, which, on reduction, yields an aminophenylarsonic acid isomeric with the atoxyl acid. The isomeride is probably a meta-derivative; unlike atoxyl, it retains its arsenic on boiling with hydriodic acid. In the para-series the arsenic is replaced by iodine.<sup>98</sup>

The arsenic in these compounds is not removed by boiling with aqueous alkali hydroxides, but when fused with these reagents it is eliminated as alkali arsenate.

The alkyl esters of arsenious acid,  $\text{As}(\text{OEt})_3$ , etc., may be obtained by heating arsenious oxide with the primary alcohols in the presence

<sup>94</sup> *Trans.*, 1908, **93**, 1180.

<sup>95</sup> G. T. Morgan and F. M. G. Micklethwait, *ibid.*, 2144,

<sup>96</sup> A. Michaelis, *Ber.*, 1908, **41**, 1514; *A.*, i, 590.

L. Benda and R. Kahn, *ibid.*, 1672, 3859; *A.*, i, 591.

A. Berthelm, *ibid.*, 1455; *A.*, i, 590.

of an insoluble dehydrating agent (for example, dry copper sulphate).<sup>99</sup>

When arsenious oxide is added to an ethereal solution of magnesium phenyl bromide, it is found to undergo the Grignard reaction, with the production, after about thirty minutes, of diphenylarsine oxide,  $[\text{As}(\text{C}_6\text{H}_5)_2]_2\text{O}$ . Prolonged treatment leads to the formation of triphenylarsine,  $\text{As}(\text{C}_6\text{H}_5)_3$ . The tri-*p*-tolylarsine,  $\text{As}(\text{C}_6\text{H}_4\cdot\text{CH}_3)_3$ , is similarly prepared, but in this case is unaccompanied by the oxide.<sup>1</sup> Magnesium benzyl bromide gives rise to dibenzylarsine hydroxide,  $\text{As}(\text{CH}_2\cdot\text{C}_6\text{H}_5)_2\cdot\text{OH}, \text{H}_2\text{O}$ .

### *Silicon Compounds.*

The chemistry of silicon derivatives offers many points for comparison with that of carbon compounds of similar structure, remarkable similarities and equally striking differences of behaviour being observed. Thus the silicones, the silicon analogues of the ketones, are not only compounds of considerable molecular complexity, tending to form molecules of the form  $(\text{R}_2\text{SiO})_3$  and boiling at very high temperatures, but they are not reduced by the usual reagents for reducing ketones, and do not form oximes or phenylhydrazones. The latter circumstance may be due to the readiness with which the Si-N linking is broken by water. Benzylethylsilicone,  $\text{C}_6\text{H}_5\cdot\text{CH}_2\text{C}_2\text{H}_5\text{Si}\cdot\text{O}$ , is prepared with ease by the action of water on benzylethylsilicon dichloride. Two isomeric dibenzylsilicols,  $\text{Si}(\text{CH}_2\cdot\text{C}_6\text{H}_5)_2(\text{OH})_2$ , were obtained, differing considerably in stability, but both yielding the silicone by loss of water. The nature of the isomerism remains unexplained, and other results which have been obtained suggest that the isomerism of silicon-oxygen compounds may prove to be of a nature not hitherto encountered amongst carbon compounds.<sup>2</sup>

Stereoisomeric silicon compounds of such optical activity as to leave no doubt as to the occurrence of optical antipodes in this series, have now been prepared by sulphonating benzylethylpropylsilicic oxide and the corresponding compound containing *isobutyl* in place of propyl, and crystallising the salts of the sulphonic acids with active methylhydrindamines. The sodium salts of the active *isobutyl* compounds have a molecular rotation nearly twice as great as that of the propyl compounds.<sup>3</sup>

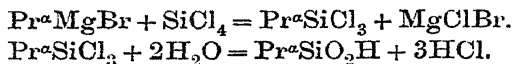
<sup>99</sup> W. R. Lang, J. F. Mackey, and R. A. Gortner, *Trans.*, 1908, 93, 1364.

<sup>1</sup> F. Sachs and H. Kantorowicz, *Ber.*, 1908, 41, 1031; *A.*, i, 1031.

<sup>2</sup> R. Robison and F. S. Kipping, *Trans.*, 1908, 93, 439.

<sup>3</sup> F. S. Kipping, *ibid.*, 457; B. D. W. Luff and F. S. Kipping, *ibid.*, 2004, 2090.

The utility of the Grignard reaction is very apparent in this work. In the researches quoted above, for instance, benzyloethylsilicon dichloride,  $\text{Si}(\text{C}_7\text{H}_7)\text{EtCl}_2$ , was caused to react with magnesium *isobutyl* bromide, giving benzyloethyl*isobutyl*silicyl chloride, which yields the required silicol or oxide on treatment with water. The siliconic acids, the analogues of the carboxylic acids, may be prepared by the action of magnesium alkyl or aryl haloids on silicon tetrachloride, and decomposition of the resulting compound with water. Thus silico-butyric acid (propylsiliconic acid) is prepared by the following reactions:



The trichlorides form ortho siliconic esters with alcohol.<sup>4</sup>

These esters may also be prepared by the action of magnesium organic haloids on ethyl orthosilicate,  $\text{Si}(\text{OEt})_4$ , but it is only possible to replace one ethoxyl group by this process. In this way, various aryl-substituted orthosiliconic esters, such as the xylyl and  $\alpha$ -naphthyl derivatives, have been prepared, yielding siliconic acids when decomposed with water.<sup>5</sup>

Silicochloroform reacts with aniline in benzene solution to form trianilinosilicon hydride,  $\text{SiH}(\text{NHPh})_3$ . This compound is useful as a source of siliciodoform, which is obtained from it in good yield by the action of hydrogen iodide in benzene solution.<sup>6</sup>

### *Sulphur Compounds.*

The properties of the organic derivatives of sulphur present many points of interest, and it is not surprising that the number of researches dealing with these substances is on the increase. The isomerism and tautomerism of many of them has an important bearing on a department of chemistry which still remains very obscure, namely, the structural arrangement of inorganic compounds.

The action of alkalis on sodium alkyl thiosulphates has previously been little investigated. The principal action appears to be the formation of the disulphide:  $2\text{R}\cdot\text{S}_2\text{O}_3\text{Na} \longrightarrow \text{R}_2\text{S}_2$ . It is not necessary, for the preparation of the disulphide, that the thiosulphate should be isolated. Thus the product of the action of *p*-nitrobenzyl chloride on sodium thiosulphate, when treated with sodium carbonate, yields di-*p*-nitrobenzyl disulphide directly.<sup>7</sup> The same is true of

<sup>4</sup> W. Melzer, *Ber.*, 1908, 41, 3390; *A.*, i, 967.

<sup>5</sup> E. Khotinsky and B. Seregenkoff, *ibid.*, 2946; *A.*, i, 1032.

<sup>6</sup> O. Ruff, *ibid.*, 3738; *A.*, i, 966.

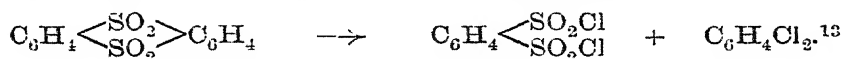
<sup>7</sup> T. S. Price and D. F. Twiss, *Trans.*, 1908, 93, 1395, 1401.

alkyl compounds, and the substance obtained in solution by Gutmann<sup>8</sup> from sodium ethyl thiosulphate, and supposed by him to be EtSOH, is diethyl disulphide. Other disulphides may be better prepared by the electrolytic oxidation of thiosulphates, dithiodiglycollic esters, for instance, being prepared in this way.<sup>9</sup>

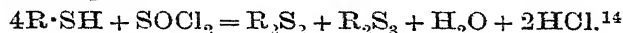
Certain disulphides, such as benzyl disulphide and 4:4'-dithioacetanilide, are found to occur in two isomeric modifications, of which one is converted into the other by the action of light.<sup>10</sup> The nature of this isomerism remains unexplained.

The oxidation of sulphides to sulphoxides is most satisfactorily performed by means of hydrogen peroxide, both for aromatic<sup>11</sup> and fatty compounds. Thus thionydiglycollic acid,  $\text{SO}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$ , is prepared in this way from thiodiglycollic acid.<sup>12</sup>

The constitution of thianthren (diphenylene disulphide) has been definitely proved to be that of an ortho-compound, by oxidation to the disulphone and treatment with phosphorus pentachloride, the products being benzene-*o*-disulphonyl chloride and *o*-dichlorobenzene:



Organic polysulphides, unlike their inorganic analogues, are not readily prepared by the action of sulphur on alkyl mercaptides, oxidation taking place. They are obtained in certain cases by the action of sulphur on disulphides in absolute alcoholic solution, saturated with anhydrous ammonia, but quantitative yields of trisulphides are obtained by the action of thionyl chloride on mercaptans according to the equation



The di- and tri-sulphides are separated by fractional distillation. The tetrasulphide of acetic acid is obtained by the action of sulphur chloride on thiolacetic acid in ethereal solution.

Sulphination, or the introduction of sulphinic groups into aromatic compounds, is carried out by passing sulphur dioxide into a mixture of the compound to be sulphinated with aluminium chloride. This method has been described independently by two groups of workers.<sup>15</sup> The process is accelerated by passing in hydrogen chloride simul-

<sup>8</sup> A. Gutmann, *Ber.*, 1908, **41**, 1650; *A.*, **1**, 497.

<sup>9</sup> T. S. Price and D. F. Twiss, *Trans.*, 1908, **93**, 1615.

<sup>10</sup> O. Hinsberg, *Ber.*, 1908, **41**, 626; *A.*, **1**, 257.

<sup>11</sup> *Ibid.*, 2836; *A.*, **1**, 875.

<sup>12</sup> M. Gazdar and S. Smiles, *Trans.*, 1908, **93**, 1833.

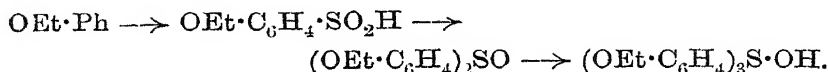
<sup>13</sup> J. J. B. Deuss, *Ber.*, 1908, **41**, 2329; *A.*, **1**, 635.

<sup>14</sup> B. Holmberg, *Annalen*, 1908, **359**, 81; *A.*, **1**, 308.

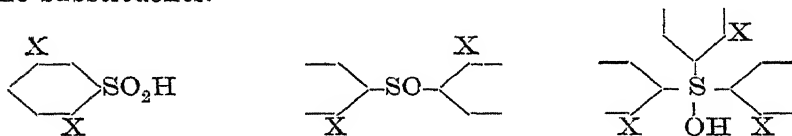
<sup>15</sup> S. Smiles and R. Le Rossignol, *Trans.*, 1908, **93**, 745; E. Knoevenagel and J. Kenner, *Ber.*, 1908, **41**, 3315; *A.*, **1**, 970.



taneously with the sulphur dioxide. The work of Smiles and Le Rossignol has led to the recognition of interesting steric influences in this reaction. The sulphination will continue beyond the stage of the sulphinic acid to those of the sulfoxide and the sulphonium compound, the process being, in the case of phenetole :



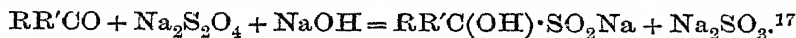
The group enters the same position as the sulphonic group in sulphonation. How far the reaction will proceed is dependent on two factors, the directive influence of such groups as ethoxyl, and steric hindrance by accumulation of ortho-substituents. Thus, with phenetole, the sulphinic group enters the para-position, and there being no ortho-substituents, the reaction proceeds to the formation of the sulphonium compound. In the ethers of quinol, sulphination takes place in the ortho-position, and progress beyond the sulphinic acid stage is rendered difficult, and almost impossible, by accumulation of ortho-substituents.



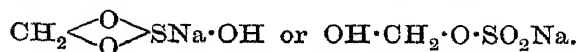
The relative influence of the two factors has been investigated in several cases.

The constitution of the aromatic sulphinic acids has been further studied by the examination of their oxidation products.<sup>16</sup> Potassium permanganate, in glacial acetic acid, converts them into  $\alpha$ -disulphones, which are identical with those obtained by the combination of sulphonyl chlorides with sodium arylsulphinates. This indicates that the acids react as  $\text{R} \cdot \text{S}^{\text{VI}}\text{O}_2 \cdot \text{H}$ , and not as  $\text{R} \cdot \text{S}^{\text{IV}}\text{O} \cdot \text{OH}$ . The  $\alpha$ -disulphones, such as  $\text{C}_6\text{H}_5 \cdot \text{SO}_2 \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_5$ , are stable, rather inert substances, only decomposed by hot concentrated alkalis.

Aldehydes and ketones react with alkaline sodium hyposulphite, forming compounds which appear to be esters of sulphylic acid,



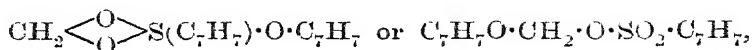
The sodium formaldehydesulphoxylate, known commercially as rongalite, probably has one of the two following structures :



<sup>16</sup> T. P. Hilditch, *Trans.*, 1908, **93**, 1524.

<sup>17</sup> E. Fromm, *Ber.*, 1908, **41**, 3397 ; *A.*, i, 968.

It forms a dibenzyl derivative,



with benzyl chloride.

Sodium thiosulphate and formaldehyde react to form thioformaldehyde, which assumes the termolecular form,  $(\text{CH}_2\text{S})_3$ .<sup>18</sup>

A few organic selenium and tellurium compounds have been prepared. A similar method to that employed for the preparation of sulphonium compounds leads to the formation of selenonium derivatives, namely, the condensation of phenolic ethers with selenium dioxide in presence of aluminium chloride. The selenonium bases are very stable, their salts are hardly acted on by sodium hydroxide, but yield hydroxides with silver oxide.<sup>19</sup>

Di- $\alpha$ -naphthyl selenide and telluride,  $(\text{C}_{10}\text{H}_7)_2\text{Se}$  and  $(\text{C}_{10}\text{H}_7)_2\text{Te}$ , and similar compounds have been prepared by the action of selenium or tellurium on mercury dinaphthyl and its analogues.<sup>20</sup>

Many of the researches not recorded in this Report, although of great importance, are omitted because they represent intermediate stages in the attack on one of the outstanding problems of this branch of chemistry. At this point it is often impossible to correlate and explain concisely the different lines along which the attack is being directed. But when success has been attained, it will then be found that these investigations will fall naturally into their places in the records of future reporters as necessary steps in the execution of another noteworthy achievement of organic analysis or synthesis.

CECIL H. DESCH.

GILBERT T. MORGAN.

<sup>18</sup> L. Vanino, *J. pr. Chem*, 1908, [ii], **77**, 367; *A.*, i, 318.

<sup>19</sup> T. P. Hilditch and S. Smiles, *Trans.*, 1908, **93**, 1384.

<sup>20</sup> R. E. Lyons and G. C. Bush, *J. Amer. Chem. Soc.*, 1908, **30**, 831; *A.*, i, 417.

## ANALYTICAL CHEMISTRY.

IN presenting this Report of the year's work in analytical chemistry, the writer wishes to emphasise the fact that, from the nature of the subject, it is scarcely possible to fulfil the object of the "Reports" as set forth in the "Introduction" to Vol. I. (1904). In the first place, the text must necessarily be somewhat disjointed, since, in the particular branch of chemistry under review, it is much more difficult than in others to construct a connected narrative, for prominence can seldom be given to any particular researches which tend to advance our knowledge of the subject as a whole. The broad reasons for this are not far to seek. Although there are some notable exceptions, it cannot be denied that the number of papers found in journals devoted to analysis in which new chemical principles are brought forward is but few, the greater part of the literary matter which has to be perused in writing a review on analytical chemistry dealing with what may at best be described as improvements rather than original discoveries. Moreover, among this majority are to be found some communications which are not only valueless but actually misleading. For these reasons, therefore, as well as from the fact that this report makes no attempt at being exhaustive, it is obvious that some selection must be made, and—apart from his own experience—the writer has based his selection on the internal evidence contained in each paper. In so voluminous and widely disseminated a literature, it is possible, indeed probable, that several deserving contributions to the subject may not have received notice, either from inadvertence or errors in judgment, but it is hoped that these omissions may amount to a minimum, and that a judicious selection has been made.

In connexion with research in analytical chemistry, it may be mentioned that an important step has been taken by the "Society of Public Analysts and Other Analytical Chemists" in inaugurating a scheme for the investigation of analytical processes and of problems in analytical chemistry, and also for the revision of published methods and their extended study when desirable. Under

this scheme it is suggested that the investigations might be undertaken by some of the senior students working in the larger colleges and teaching institutions, and a fund has been established by the above Society for defraying incumbent expenses. The only conditions are that accounts of the researches are to be published (subject to the approval of the Editorial Committee) in *The Analyst*, and, when possible, to be brought before the Society in the form of communications.<sup>1</sup>

### *Inorganic Chemistry.*

*Qualitative.*—The system of qualitative analysis, the first two papers on which were published last year by A. A. Noyes and W. C. Bray,<sup>2</sup> has been further developed by A. A. Noyes, W. C. Bray, and E. B. Spear.<sup>3</sup> This third communication deals with the metals of the ammonium sulphide group. It is impossible to review such a paper as a whole, covering as it does some eighty pages, but among other things the authors show that when the precipitate obtained with ammonia and ammonium sulphide is dissolved in acid, and the solution boiled with a mixture of sodium peroxide, hydroxide, and carbonate, the members of the iron group, including nickel, cobalt, thallium, manganese, titanium, and zirconium, are precipitated, whilst those of the aluminium group, including glucinum, zinc chromium, uranium, and vanadium, remain in solution as sodium salts. A somewhat similar scheme, involving the use of hydrogen peroxide and sodium hydroxide, is suggested by E. Ebler.<sup>4</sup> H. Caron and D. Raquet<sup>5</sup> suggest sodium peroxide as a reagent for the separation of the elements of group III in presence of phosphates. The same compound is recommended by D. F. Calhane<sup>6</sup> for the detection of chromium in presence of iron; the oxidation proceeds to the perchromate stage. For the rapid qualitative analysis of a mineral, W. B. Pollard's<sup>7</sup> process consists in fusing it with vaselin and sodium peroxide. The more positive elements remain in the melt as insoluble oxides and carbonates, whilst the others exist in the highest state of oxidation as soluble sodium salts; special tests must be made for mercury (on account of its volatility) and for sodium. J. H. Walton, jun., and H. A. Scholz<sup>8</sup> describe a method for decomposing certain slags and

<sup>1</sup> *Analyst*, 1908, **33**, 41.

<sup>2</sup> *J. Amer. Chem. Soc.*, 1907, **29**, 137; *A.*, 1907, ii, 391.

<sup>3</sup> *Ibid.*, 1908, **30**, 481; *A.*, ii, 538.

<sup>4</sup> *Zeitsch. anal. Chem.*, 1908, **47**, 665; *A.*, ii, 987.

<sup>5</sup> *Bull. Soc. chim.*, 1908, [iv], **3**, 622; *A.*, ii, 630.

<sup>6</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 770; *A.*, ii, 630.

<sup>7</sup> *Chem. News*, 1908, **98**, 211; *A.*, ii, 1069.

<sup>8</sup> *Amer. Chem. J.*, 1908, **39**, 771; *A.*, ii, 732.

sulphide ores, which consists in fusing them with a mixture of sodium peroxide, zinc sulphide, and potassium persulphate.

In order to detect helium in minerals, F. Bordas<sup>9</sup> heats the substance, and passes the gas through a Dewar's charcoal tube; the helium is much less readily absorbed than other gases, and may be detected spectroscopically.

E. Selvatici<sup>10</sup> advocates the use of thioacetic acid instead of hydrogen sulphide for the precipitation of the metals of group II. He also gives a scheme of separation obviating the use of ammonium sulphide. H. Bollenbach<sup>11</sup> makes use of ammonium persulphate in separating the metals of group II. G. D. Lander and H. W. Winter<sup>12</sup> deal with the detection of poisonous metals.

L. Tschugaeff<sup>13</sup> has pointed out that Pozzi-Escot's molybdate method of detecting nickel<sup>14</sup> is less sensitive than his own dimethylglyoxime method.<sup>15</sup> Pozzi-Escot<sup>16</sup> has modified his molybdate method, and more recently<sup>17</sup> he has described conditions whereby cobalt may be detected in the presence of 1000 times its amount of nickel. H. Grossmann and B. Schück<sup>18</sup> state that this method had been previously described by Marckwald; they also state that as a test for nickel in the presence of cobalt it is less delicate than their own,<sup>19</sup> besides which there is a tendency for the precipitation of cobalt as the violet molybdate.<sup>20</sup> H. Grossmann and W. Heilborn<sup>21</sup> suggest the use of dicyanodiamidine for the simultaneous detection of nickel and cobalt. The former metal gives a crystalline precipitate,<sup>22</sup> and the latter an intense reddish-violet coloration.<sup>23</sup>

W. Neumann<sup>24</sup> describes an electrolytic method whereby 0.008 milligram of zinc in 0.1 c.c. of solution may be detected. L. W. McKay<sup>25</sup> draws attention to the danger of zinc sulphide re-dissolving when precipitated in presence of sodium hydroxide.

<sup>9</sup> *Compt. rend.*, 1908, 146, 628; *A.*, ii, 430.

<sup>10</sup> *Boll. chim. farm.*, 1908, 47, 73; *A.*, ii, 322.

<sup>11</sup> *Zeitsch. anal. Chem.*, 1908, 47, 690; *A.*, ii, 984.

<sup>12</sup> *Analyst*, 1908, 33, 450; *A.*, 1909, ii, 95.

<sup>13</sup> *Compt. rend.*, 1907, 145, 697; *A.*, 1907, ii, 989.

<sup>14</sup> *Ann. Report*, 1907, 200.

<sup>15</sup> *Ber.*, 1905, 38, 2520; *A.*, 1905, ii, 613; Kraut, *Zeitsch. angew. Chem.*, 1906, 19, 793; *A.*, 1906, ii, 858; Brunck, *Ann. Report*, 1907, 205.

<sup>16</sup> *Ann. Chim. anal.*, 1908, 13, 16; *A.*, ii, 133.

<sup>17</sup> *Ibid.*, 390; *A.*, ii, 988.

<sup>18</sup> *Bull. Soc. chim.*, 1908, [iv], 3, 14; *A.*, ii, 230.

<sup>19</sup> *Ber.*, 1906, 39, 3356; *A.*, 1906, ii, 908.

<sup>20</sup> See, further, *Chem. Zeit.*, 1908, 32, 804; *Bull. Soc. chim.*, 1908, [iv], 3, 894; *A.*, ii, 899. <sup>21</sup> *Ber.*, 1908, 41, 1878; *A.*, ii, 635. <sup>22</sup> *Ann. Report*, 1907, 205.

<sup>23</sup> See also H. Grossmann, *Chem. Zeit.*, 1908, 32, 315; *A.*, ii, 434.

<sup>24</sup> *Zeitsch. Elektrochem.*, 1907, 13, 751; *A.*, ii, 67.

<sup>25</sup> *J. Amer. Chem. Soc.*, 1908, 30, 376; *A.*, ii, 431.

W. Bettel<sup>26</sup> states that molybdic acid gives, with hydrogen peroxide and a trace of ammonia, a brownish-red coloration. A method for the detection of ruthenium in platinum alloys has been devised by N. A. Orloff.<sup>27</sup>

N. Schoorl<sup>28</sup> describes the appearance under the microscope of silver, lead, and mercurous chlorides, and later<sup>29</sup> that of arsenic, antimony, and tin compounds. Subsequently<sup>30</sup> he deals with the microchemical analysis of the sulphides of mercury, bismuth, lead, copper, and cadmium. In connexion with the well-known volatility of mercury compounds, K. Kof and H. Haehn<sup>31</sup> state that a moistened filter-paper placed over a 2 per cent. solution of mercuric chloride for sixty-five hours is rendered black on treatment with hydrogen sulphide; also that a distinct white patch is obtained on developing a photographic plate which has been kept for twenty-four hours at a distance of 2 to 3 mm. from a drop of a 0.01 per cent. solution of mercuric chloride.<sup>32</sup> J. Moir<sup>33</sup> gives two methods for the detection of mercuric chloride in nitrocellulose.

According to M. Delépine,<sup>34</sup> one part of copper in 1,000,000 can be detected by the brown coloration produced with a solution of a dialkyldithiocarbamate. Iron gives a pink colour with this reagent; nickel and cobalt also give colours. E. Knecht<sup>35</sup> shows that when titanous sulphate is added to a solution of a copper salt (limit one part of copper per 1,000,000), metallic copper separates. A. W. Gregory<sup>36</sup> states that 0.01 milligram of silver may be detected by the brown colour produced on addition of ammonium salicylate and persulphate. W. J. Karslake's method for the detection of manganese and chromium in mixtures<sup>37</sup> consists in boiling the solution in nitric or sulphuric acid with ammonium persulphate and silver nitrate, when permanganate and perchromate are formed. When shaken with hydrogen peroxide and ether, the former is decomposed, whilst the latter dissolves in the ether with the production of the well-known blue colour.

H. Caron and D. Raquet<sup>38</sup> point out that in the well-known method of detecting barium in presence of strontium and calcium,

<sup>26</sup> *Chem. News*, 1908, **97**, 40; *A.*, ii, 230.

<sup>27</sup> *Chem. Zeit.*, 1908, **32**, 77; *A.*, ii, 231.

<sup>28</sup> *Zeitsch. anal. Chem.*, 1908, **47**, 209; *A.*, ii, 432.

<sup>29</sup> *Ibid.*, 367; *A.*, ii, 777.

<sup>30</sup> *Ibid.*, 729; *A.*, 1909, ii, 96.

<sup>31</sup> *Arch. Pharm.*, 1907, **245**, 529; *A.*, ii, 69.

<sup>32</sup> Compare *Zeitsch. physikal. Chem.*, 1907, **60**, 367; *A.*, 1907, ii, 732.

<sup>33</sup> *Chem. News*, 1908, **97**, 133.

<sup>34</sup> *Bull. Soc. chim.*, 1908, [iv], **3**, 652; *A.*, ii, 633.

<sup>35</sup> *Ber.*, 1908, **41**, 498; *A.*, ii, 270.

<sup>36</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 905; *A.*, ii, 635.

<sup>37</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 905; *A.*, ii, 635.

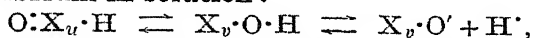
<sup>38</sup> *Bull. Soc. chim.*, 1908, [iv], **3**, 483; *A.*, ii, 496.

the addition of hydrofluosilicic acid sometimes leads to the deposition of gelatinous silica, which may be mistaken for barium silicofluoride. They show<sup>39</sup> that barium may be eliminated from strontium salts by fractional precipitation by alkali chromates.

J. Milbauer<sup>40</sup> states that neodymium gives a colourless borax bead in the oxidising, and a violet in the reducing, flame, whilst praseodymium gives a yellowish-green bead in the oxidising, and a green in the reducing, flame. O. Lutz<sup>41</sup> points out that borax beads are to be preferred for the detection of positive, and phosphate beads for negative, ions. J. Donau<sup>42</sup> describes a delicate method of detecting gold, platinum, and silver by means of the metaphosphate bead.

For the detection of phosphates in minerals, A. P. Lidoff<sup>43</sup> heats the finely-powdered mineral first alone, and then with magnesium or a mixture of it and aluminium; the fusion is gently warmed with 20 per cent. sodium hydroxide solution, the evolved gases being brought in contact with copper sulphate paper. The formation of copper phosphide (black coloration) indicates the presence of phosphorus. J. S. Jamieson<sup>44</sup> describes a test for bromides.

*Quantitative.*—An important contribution to the theory of indicators is that of J. T. Hewitt,<sup>45</sup> who points out the insufficiency of the ionic theory alone in explaining the colour changes of phenolphthalein, and concludes that the assumption of tautomeric change must also be made. In the light of A. G. Green's experiments,<sup>46</sup> Hewitt assumes that this and like indicators obey the following equilibrium in solution:



where  $X_u$  and  $X_v$  are isomeric radicles. These considerations led him to recommend *p*-nitrobenzeneazo- $\alpha$ -naphthol as an indicator. It yields results similar to phenolphthalein when used for the titration of alkali hydroxides with weak acids, the colour change being from purple to yellow. The view that phenolphthalein exhibits tautomerism was put forward by S. F. Acree in 1904, but was denied by J. Stieglitz. Acree's latest hypothesis<sup>47</sup> commends itself, however, to Stieglitz.<sup>48</sup> A. Hantzsch and F. Hilscher<sup>49</sup> bring

<sup>39</sup> *Bull. Soc. chim.*, 1908, [iv], 3, 493; *A.*, ii, 496.

<sup>40</sup> *Zeitsch. anal. Chem.*, 1907, 46, 657; *A.*, ii, 70.

<sup>41</sup> *Ibid.*, 1908, 47, 1; *A.*, ii, 226.

<sup>42</sup> *Zeitsch. Chem. Ind. Kolloide*, 1908, 2, 273; *A.*, ii, 434.

<sup>43</sup> *J. Russ. Phys. Chem. Soc.*, 1908, 40, 817; *A.*, ii, 894.

<sup>44</sup> *Proc.*, 1908, 24, 144.

<sup>45</sup> *Analyst*, 1908, 33, 85; *A.*, i, 269.

<sup>46</sup> *Ber.*, 1907, 40, 3724; *J. Soc. Chem. Ind.*, 1908, 27, 4; *A.*, 1907, i, 933.

<sup>47</sup> *Amer. Chem. J.*, 1908, 39, 528, 649; *A.*, i, 422, 652.

<sup>48</sup> *Ibid.*, 651; *A.*, i, 652; compare *Ibid.*, 789; *A.*, i, 653.

<sup>49</sup> *Ber.*, 1908, 41, 1187; *A.*, i, 469.

forward evidence that helianthin, in the solid state, has a quinonoid structure, but that in aqueous solution it exists as an aminoazo- and sulphonic acid-form in equilibrium, whilst its sodium salt (methyl-orange) is a sulphonate both in the solid state and in solution. J. H. Hildebrand<sup>50</sup> has applied the König spectrophotometer to the measurement of the dissociation constant of phenolphthalein dissolved in aqueous solutions of ammonia and ammonium chloride, in which the concentration of the hydrogen ions is known. It is found to be  $1.7 \times 10^{-10}$  for solutions in which 5 to 65 per cent. of the phenolphthalein is dissociated.<sup>51</sup> M. Barberio<sup>52</sup> has described a new indicator, "resorubin," obtained by the action of nitrous acid on resorcinol; the violet neutral solution becomes blue with alkalis or yellow with acids. It is said to resemble lacmoid, but to be more sensitive in presence of ammonium salts. E. Rupp and R. Loose<sup>53</sup> propose *p*-dimethylaminoazobenzene-*o*-carboxylic acid as an indicator which may be used for the titration of weak bases such as alkaloids; it can be used to titrate ammonia even in *N*/100-solution. To distinguish mineral from organic acids, E. Linder<sup>54</sup> employs metanil-yellow paper, which (with the former only) becomes violet. A. B. Lyons<sup>55</sup> recommends hæmatoxylin for titrating phosphoric acid. J. K. Wood<sup>56</sup> has carefully determined the basic and acidic constants of arsenious and aluminium hydroxide. V. H. Veley's paper on the affinity constants of bases, as determined by the aid of methyl-orange,<sup>57</sup> is of interest to analytical chemists. S. P. L. Sørensen and A. C. Andersen<sup>58</sup> give some useful hints on Winkler's method of estimating hydroxides in presence of carbonates.<sup>59</sup> L. Clarke and C. L. Jackson<sup>60</sup> show that rosocyanin, the substance which is produced in the test for boric acid with turmeric paper, is an isomeride of curcumin,  $C_{14}H_{14}O_2$ .

In connexion with halogen derivatives, P. Jannasch<sup>61</sup> has continued his studies on the separation of the halogens by means of hydrogen peroxide.<sup>62</sup> In its present form, his method is quantitative, good results being obtained for chlorine and iodine, whilst those for bromine are slightly low. H. Baubigny<sup>63</sup> has modified Hager's

<sup>50</sup> *Zeitsch. Elektrochem.*, 1908, **14**, 349; *A.*, ii, 646.

<sup>51</sup> Compare R. Wegscheider and A. Schugowitsch, *Ibid.*, 510; *A.*, ii, 806.

<sup>52</sup> *Gazzetta*, 1907, **37**, ii, 577; *A.*, i, 161.

<sup>53</sup> *Ber.*, 1908, **41**, 3905; *A.*, 1909, ii, 90.

<sup>54</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 485; *A.*, ii, 627.

<sup>55</sup> *Pharm. Rev.*, 1908, **26**, 97; *A.*, ii, 532.

<sup>56</sup> *Trans.*, 1908, **93**, 411.

<sup>57</sup> *Ibid.*, 652.

<sup>58</sup> *Zeitsch. anal. Chem.*, 1908, **47**, 279; *A.*, ii, 534.

<sup>59</sup> Compare also Andersen, *Tidsskr. Kem. Farm. Therapt*, 1908, **11**, 161; *A.*, ii, 985.

<sup>60</sup> *Amer. Chem. J.*, 1908, **39**, 696; *A.*, i, 670.

<sup>61</sup> *J. pr. Chem.*, 1908, [ii], **78**, 28; *A.*, ii, 730.

<sup>62</sup> *Ann. Report*, 1906, 203.

<sup>63</sup> *Compt. rend.* 1908, **146**, 335; *A.*, ii, 321.



method of separating silver halides.<sup>64</sup> When only the chloride and iodide are present, these may be separated quantitatively by treatment at 70—80° with a solution containing 10 grams of ammonium sesquicarbonate and 20 c.c. of 20 per cent. ammonia per litre; this dissolves the silver iodide only. B. H. Buttle and J. T. Hewitt<sup>65</sup> have studied the solubility of silver chloride in mercuric nitrate solution, and arrive at the same conclusion as Morse,<sup>66</sup> that when mercuric nitrate is present in large excess, chlorine only occurs as HgCl ions. For the determination of fluorine in rocks, etc., in quantities up to 3 per cent., G. Steiger<sup>67</sup> makes use of the fact that fluorides bleach the coloration produced by hydrogen peroxide and titanium. As this is not a linear function, reference is made to a curve. The presence of aluminium salts and phosphates influence the results, which, however, are in no case trustworthy when as much as 10 per cent. of fluorine is present. B. Carlson and J. Gelhaar<sup>68</sup> deal with the detection and estimation of chlorites and hypochlorites in chlorates. E. Knecht<sup>69</sup> has devised a volumetric method for the estimation of chlorates. D. Venditori<sup>70</sup> makes the interesting observation that, in presence of sulphuric acid, chlorates but not perchlorates are reduced by finely-divided aluminium. Grützner's method of determining chlorates and bromates by heating with formaldehyde, nitric acid, and silver nitrate<sup>71</sup> has been extended to iodates and periodates by H. Brunner and R. Mellet.<sup>72</sup> To prevent loss of free halogen, and to obviate working in a closed vessel, potassium persulphate is added to the reaction mixture. H. Baubigny<sup>73</sup> shows that an ammoniacal solution of silver chloride or bromide, when heated with iodic acid, only deposits silver iodide when a temperature of 200° is reached.

Use has been made of sodium peroxide by S. W. Parr<sup>74</sup> in the estimation of sulphur in pyrites, coal, and indiarubber. Pyrites is mixed with sodium peroxide, potassium chlorate, and benzoic acid, and the mixture ignited in a special bomb; the melt contains the sulphur as sulphate. A special mixture appears to be required

<sup>64</sup> *Zeitsch. anal. Chem.*, 1871, **10**, 341.

<sup>65</sup> *Trans.*, 1908, **93**, 1405.

<sup>66</sup> *Zeitsch. physikal. Chem.*, 1902, **41**, 709; *A.*, 1903, ii, 12.

<sup>67</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 219; *A.*, ii, 426.

<sup>68</sup> *Chem. Zeit.*, 1908, **32**, 604, 633; *A.*, ii, 731.

<sup>69</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 434; *A.*, ii, 627.

<sup>70</sup> *Gazzetta*, 1907, **37**, ii, 383; *A.*, ii, 63.

<sup>71</sup> *Arch. Pharm.*, 1896, **234**, 634; *A.*, 1897, ii, 166.

<sup>72</sup> *J. pr. Chem.*, 1908, [ii], **77**, 33; *A.*, ii, 222.

<sup>73</sup> *Compt. rend.*, 1908, **146**, 1097; *A.*, ii, 577.

<sup>74</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 764; *A.*, ii, 628.

for each substance. Carbon in carborundum may be estimated (as carbonate) by heating the sample in this way with sodium peroxide and "boro-magnesium" mixture.<sup>75</sup> The results quoted are satisfactory (see also under Organic Chemistry). E. Jaboulay<sup>76</sup> describes a volumetric method for estimating sulphur in steel. For a detailed study of the various methods for this purpose, M. Orthey's paper<sup>77</sup> may be consulted. According to H. Kiliani,<sup>78</sup> when alkali thiosulphate is titrated in alkaline solution with permanganate, as in Reinige's method of estimating iodides,<sup>79</sup> sulphate and not tetrathionate is formed, hence 8 mols. of permanganate require 3 mols. of thiosulphate for decomposition. V. Lenher<sup>80</sup> shows that in the method of estimating tellurium by precipitation with hydrazine,<sup>81</sup> it is an advantage if the solution contains sulphurous acid; the results are accurate.

As usual, a great many papers have appeared during the year dealing with the estimation of phosphorus and phosphates. F. W. Hinrichsen<sup>82</sup> has confirmed the accuracy of H. Lidholm's process<sup>83</sup> for the estimation of phosphorus in calcium carbide. An accurate method for the estimation of phosphorus in phosphor-tin has been devised by W. Gemmell and S. L. Archbutt.<sup>84</sup> F. Repiton<sup>85</sup> describes a modification of Malot's method of estimating phosphoric acid by titration with uranic solution, employing cochineal, *in situ*, as indicator; the results are shown to be satisfactory. For the estimation of phosphorus in iron, etc., G. Chesneau<sup>86</sup> weighs the ammonium phosphomolybdate precipitate, and states conditions whereby this compound may be precipitated in presence of ammonium nitrate containing constantly 1.6 per cent. of phosphorus. With reference to the estimation of phosphoric acid as ammonium phosphomolybdate,<sup>87</sup> G. von Knorre,<sup>88</sup> adverting to his previous statement that tungstic acid may be separated from phosphoric acid almost quantitatively by precipitation with benzidine hydrochloride, points out that the results are vitiated by the insol-

<sup>75</sup> *Loc. cit.*      <sup>76</sup> *Rev. gen. chim. pure appl.*, 1907, **10**, 193; *A.*, ii, 223.

<sup>77</sup> *Zeitsch. angew. Chem.*, 1908, **21**, 1359, 1393; *A.*, ii, 731.

<sup>78</sup> *Chem. Zeit.*, 1908, **32**, 1018; *A.*, ii, 982

<sup>79</sup> *Zeitsch. anal. Chem.*, 1870, **9**, 39.

<sup>80</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 388; *A.*, ii, 426.

<sup>81</sup> Gutbier, *Ber.*, 1901, **34**, 2724; *A.*, 1901, ii, 687.

<sup>82</sup> *Mitt. K. Materialprüfs-Amt. Gross. Lichterfelde West*, 1907, **25**, 110; *A.* 1908, ii, 131.

<sup>83</sup> *Zeitsch. angew. Chem.*, 1904, **17**, 1452; *A.*, 1904, ii, 776.

<sup>84</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 427; *A.*, ii, 629.

<sup>85</sup> *Mon. Sci.*, 1907, [iv], **21**, ii, 753, 815; *A.*, ii, 320, 428.

<sup>86</sup> *Compt. rend.*, 1908, **146**, 758; *A.*, ii, 427.

<sup>87</sup> Compare P. Christensen, *Zeitsch. anal. Chem.*, 1908, **47**, 529; *A.*, ii, 895; E. Raben, *ibid.*, 546; *A.*, ii, 896.      <sup>88</sup> *Ibid.*, 37; *A.*, ii, 231.

bility of benzidine phosphate in water, but he shows that the separation is quantitative when the homologous tolidine hydrochloride is employed.

In connexion with the estimation of carbon in iron and steel, M. Orthey<sup>89</sup> shows that the combustion method in a current of oxygen in presence of bismuth oxide gives good results. L. L. de Koninck and E. von Winiwarter<sup>90</sup> propose to burn the substance with lead borate in a current of oxygen. H. Isham and J. Aumer<sup>91</sup> show that when iron or steel is ignited in a current of oxygen alone, the carbon (but not the sulphur) is almost completely burnt. C. M. Johnson<sup>92</sup> describes an electric furnace for the estimation of carbon in iron, etc. New apparatus for the moist method have been devised by M. Widemann<sup>93</sup> and by T. Grzeschik.<sup>94</sup> E. P. Moore and J. W. Bain<sup>95</sup> show that during the solution of steel in potassium cupric chloride there may be a loss of 0.4—0.5 milligram of carbon per gram of steel. In titrating lead with sodium sulphide, H. Koch<sup>96</sup> adds carbon tetrachloride to cause the subsidence of the precipitate. Some useful data on the colorimetric estimation of lead as sulphide are given by H. W. Woudstra.<sup>97</sup> Several papers dealing with the assay of red lead have been published during the year.<sup>98</sup> The last-mentioned shows the limit of accuracy of the various methods in use. Some useful volumetric methods of estimating mercury are described by E. Rupp,<sup>99</sup> and by the same author in conjunction with W. F. Schirmer.<sup>1</sup> For the estimation of mercuric salts, S. G. Liversedge<sup>2</sup> suggests conversion into mercuric iodide and extraction of the latter with ether; the method is particularly adapted for the estimation of small quantities of mercury. In connexion with the estimation of mercury, the volatility of its salts (see p. 183) is, as a rule, ignored by authors. J. F. Spencer and Miss M. Le Pla<sup>3</sup> have devised a very accurate method of estimating silver and thallium

<sup>89</sup> *Chem. Zeit.*, 1908, **32**, 31; *A.*, ii, 131.

<sup>90</sup> *Bull. Soc. chim. Belg.*, 1908, **22**, 104; *A.*, ii, 320.

<sup>91</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 1236; *A.*, ii, 898.

<sup>92</sup> *Ibid.*, 773; *A.*, ii, 630.

<sup>93</sup> *Zeitsch. chem. Apparatenkunde*, 1908, **3**, 296; *A.*, ii, 984.

<sup>94</sup> *Chem. Zeit.*, 1908, **32**, 1092; *A.*, ii, 1071.

<sup>95</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 845; *A.*, ii, 899.

<sup>96</sup> *Chem. Zeit.*, 1908, **32**, 124; *A.*, ii, 227.

<sup>97</sup> *Zeitsch. anorg. Chem.*, 1908, **58**, 168; *A.*, ii, 633.

<sup>98</sup> See for instance J. F. Sacher, *Chem. Zeit.*, 1908, **32**, 62; *A.*, ii, 228; E. Pieszczyk, *Pharm. Zeit.*, 1908, **53**, 87; *A.*, ii, 228; E. E. Dunlap, *J. Amer. Chem. Soc.*, 1908, **30**, 611; *A.*, ii, 537; P. Beck, *Zeitsch. anal. Chem.*, 1908, **47**, 465; *A.*, ii, 777.

<sup>99</sup> *Chem. Zeit.*, 1908, **32**, 1077; *A.*, ii, 1073.

<sup>1</sup> *Pharm. Zeit.*, 1908, **53**, 928; *A.*, ii, 1073.

<sup>2</sup> *Analyst*, 1908, **33**, 217; *A.*, ii, 634.

<sup>3</sup> *Trans.*, 1908, **93**, 858.

in mixtures. W. R. Lang and J. O. Woodhouse<sup>4</sup> describe a modification of Lang and Allen's apparatus<sup>5</sup> which may be employed for the estimation of silver by Gay-Lussac's method

G. S. Jamieson, H. L. Levy, and H. L. Wells<sup>6</sup> propose a volumetric method for the estimation of copper, which, on their evidence, has an average limit of accuracy of one in 300. The copper is precipitated as cuprous thiocyanate, and the latter, after washing, dissolved in dilute hydrochloric acid and titrated with potassium iodate and chloroform. The writer can fully confirm H. Theodor's statements<sup>7</sup> regarding the accuracy of Volhard's titration method of estimating copper; more than twenty years ago he used the method of neutralising the solution with a slight excess of ammonia before reducing with sulphurous acid for the purpose of getting rid of the nitric acid, which is now suggested by O. Kuhn.<sup>8</sup> A. K. Huntington and C. H. Desch<sup>9</sup> deal with the planimetric analysis of alloys and the structure of phosphor-copper.

The fact that when titrated with permanganate in presence of hydrochloric acid ferrous salts require more of the standard solution than is necessary for their oxidation to the ferric state has long been known. T. W. Harrison and F. M. Perkin<sup>10</sup> find that addition of manganous sulphate retards the reducing action of hydrochloric acid, but that the colour interferes with the end point of the titration. In discussing their paper, O. Hehner<sup>11</sup> quoted Fresenius's directions, and cited a paper by Loewenthal and Lenssen.<sup>12</sup> In a lengthy paper by L. Brandt,<sup>13</sup> the necessity is urged of standardising the permanganate in presence of hydrochloric acid when that acid occurs in the assay liquid. Directions are given for the preparation of ferric oxide in a state of purity, which is recommended as the best compound to use in standardising the solution; the reduction is effected by stannous chloride. In other papers on the permanganate method, M. M. P. Muir<sup>14</sup> proposes to arrest the evolution of hydrogen, when the reduction of ferric salt is accomplished with zinc, by the addition of mercuric chloride; and H. D. Newton<sup>15</sup> employs titanous sulphate as reducing agent, destroying the excess with bismuth oxide. The results quoted are

<sup>4</sup> *Trans.*, 1908, **93**, 1037.      <sup>5</sup> *Ibid.*, 1907, **91**, 1370.

<sup>6</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 760; *A.*, ii, 634.

<sup>7</sup> *Chem. Zeit.*, 1908, **32**, 889; *A.*, ii, 898.

<sup>8</sup> *Ibid.*, 1056; *A.*, ii, 1072.

<sup>9</sup> *Trans. Faraday Soc.*, 1908, **4**, 51; *A.*, ii, 846.

<sup>10</sup> *Analyst*, 1908, **33**, 43; *A.*, ii, 228.

<sup>11</sup> *Ibid.*

<sup>12</sup> *Zeitsch. anal. Chem.*, 1861, **1**, 329, 361.

<sup>13</sup> *Chem. Zeit.*, 1908, **32**, 812; *A.*, ii, 899.

<sup>14</sup> *Chem. News*, 1908, **97**, 57; *A.*, ii, 228.

<sup>15</sup> *Amer. J. Sci.*, 1908, [iv], **25**, 343; *A.*, ii, 538.

very accurate. G. Edgar<sup>16</sup> deals with the estimation of iron and vanadium in mixtures by titration with permanganate, and in another paper<sup>17</sup> he has elaborated conditions whereby vanadic and molybdic oxides may be estimated by permanganate. S. B. Jatar's method<sup>18</sup> for the estimation of iron and chromium by titration with titanous chloride appears useful and accurate. H. Bollenbach<sup>19</sup> proposed to titrate ferric salts with sodium hyposulphite ( $\text{Na}_2\text{SO}_3$ ).

For the decomposition of ferro-compounds, especially ferro-silicon, P. Nicolardot<sup>20</sup> heats with sulphur chloride. R. B. Moore and I. Miller<sup>21</sup> show that iron may be precipitated from a solution containing free hydrochloric acid by means of pyridine; aluminium, chromium, and zinc are partly precipitated, whereas manganese, nickel, and cobalt remain in solution. F. C. Mathers<sup>22</sup> shows that traces of iron may be removed from indium by precipitation from an acetic acid solution by nitroso- $\beta$ -naphthol.

According to A. W. Gregory,<sup>23</sup> one part of iron in 10,000 of copper may be detected by the red colour given by ferric salts with salicylic acid in presence of sodium acetate. He bases a colorimetric method on this reaction.

With reference to the dimethylglyoxime and dicyanodiamidine methods of estimating nickel,<sup>24</sup> O. Brunck<sup>25</sup> brings forward evidence showing the superior accuracy of the former, whilst Grossmann and Schück<sup>26</sup> uphold the dicyanodiamidine method on the ground that the nickel compound is insoluble in strong ammoniacal alkali hydroxide solutions. H. Cantoni and M. Rosenstein<sup>27</sup> propose for the volumetric estimation of nickel, titration with either ferro- or ferri-cyanide, using ferric (or uranium) or ferrous indicators respectively; the ferricyanide method with the liquid faintly acidified with acetic acid gives the better results.

In a series of papers M. E. Pozzi-Escot deals with the estimation of both nickel and cobalt by the molybdate method and the separation of these metals from others.<sup>28</sup>

<sup>16</sup> *Zeitsch. anorg. Chem.*, 1908, 59, 74.

<sup>17</sup> *Amer. J. Sci.*, 1908, [iv], 25, 232; *A.*, ii, 540.

<sup>18</sup> *J. Soc. Chem. Ind.*, 1908, 27, 673; *A.*, ii, 778.

<sup>19</sup> *Chem. Zeit.*, 1908, 32, 146; *A.*, ii, 229.

<sup>20</sup> *Compt. rend.*, 1908, 147, 676; *A.*, ii, 1074.

<sup>21</sup> *J. Amer. Chem. Soc.*, 1908, 30, 593; *A.*, ii, 434.

<sup>22</sup> *Ibid.*, 209; *A.*, ii, 434.

<sup>23</sup> *Trans.*, 1908, 93, 93.

<sup>24</sup> *Ann. Report*, 1907, 205.

<sup>25</sup> *Zeitsch. angew. Chem.*, 1907, 20, 1845; *A.*, 1907, ii, 989.

<sup>26</sup> *Ibid.*, 1981; *A.*, ii, 71.

<sup>27</sup> *Bull. Soc. chim.*, 1908, [iv], 1, 1163; *A.*, ii, 230.

<sup>28</sup> *Ann. Chim. anal.*, 1908, 13, 66; *Compt. rend.*, 1907, 145, 1334; *A.*, ii, 229; *Ann. Chim. anal.*, 1908, 13, 89; *A.*, ii, 324; *ibid.*, 85, 215, 217; *A.*, ii, 539, 540, 635.

E. D. Campbell and W. Arthur<sup>39</sup> describe a modification of Moore's volumetric method<sup>40</sup> for the estimation of nickel and chromium in steel. A. A. Blair<sup>41</sup> has worked out a scheme for the determination of vanadium, molybdenum, chromium, and nickel in steel; from the single example given, it appears to be very accurate. The estimation of vanadium in iron and steel is dealt with by E. D. Campbell and E. L. Woodhams.<sup>42</sup>

In connexion with the estimation of tin, D. B. Dott<sup>38</sup> draws attention to the solubility of metastannic acid in hydrochloric acid; he points out further that, in the analysis of ores, tin is volatilised when a solution in aqua regia is evaporated to dryness for the purpose of separating the silica.<sup>34</sup> H. Reynolds<sup>35</sup> titrates a stannous solution with dichromate, using azobenzenesulphonic acid as indicator; the restoration of the red colour of the indicator marks the end of the oxidation. E. Schürmann and W. Scharfenberg<sup>36</sup> describe a modification of Clarke's oxalic acid method for the analysis of white metal. A. Kolb and R. Formhals<sup>37</sup> show that the reaction  $\text{Sb}_2\text{O}_5 + 4\text{HI} \rightleftharpoons \text{Sb}_2\text{O}_3 + 2\text{H}_2\text{O} + 2\text{I}_2$  is practically complete from left to right if sufficient excess of hydric acid be used.

L. Rosenthaler's observations<sup>38</sup> respecting the quantitative precipitation of arsenious and arsenic acids, the former by barium chloride and ammonia and the latter by barium chloride and sodium hydroxide, are worthy of attention. H. Reckleben and G. Lockemaun<sup>39</sup> describe gravimetric, volumetric, and gasometric methods of estimating arsine in air.

P. Cazeneuve<sup>40</sup> utters a warning against the use of arseniferous dressings as insecticides in agriculture. The Gutzeit test for arsenic, antimony, and phosphorus has been rendered more conclusive by B. Sjollema.<sup>41</sup> In the case of arsenic, he states that he was able to obtain microscopical crystals with 0.005 milligram of arsenious oxide. C. H. Nieuwland,<sup>42</sup> on the other hand, was unable to

<sup>39</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 1116; *A.*, ii, 779.

<sup>40</sup> *Chem. News*, 1895, **72**, 92; *A.*, 1895, ii, 534.

<sup>41</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 1229; *A.*, ii, 900.

<sup>42</sup> *Ibid.*, 1233; *A.*, ii, 901.

<sup>38</sup> *Pharm. J.*, 1908, [iv], **27**, 486; *A.*, ii, 899.

<sup>34</sup> See further, *Ibid.*, 585; *A.*, ii, 1075.

<sup>35</sup> *Chem. News*, 1908, **97**, 13; *A.*, ii, 134.

<sup>36</sup> *Mitt. K. Materialprüfungs.-Amt.*, 1908, **25**, 270; *A.*, ii, 537.

<sup>37</sup> *Zeitsch. anorg. Chem.*, 1908, **58**, 189; *A.*, ii, 599.

<sup>38</sup> *Apoth. Zeit.*, 1907, **22**, 982; *A.*, ii, 322.

<sup>39</sup> *Zeitsch. anal. Chem.*, 1908, **47**, 126; *A.*, ii, 224.

<sup>40</sup> *Rev. intern. Falsif.*, 1908, **21**, 11.

<sup>41</sup> *Chem. Weekblad.*, 1908, **5**, 11; *A.*, ii, 431.

<sup>42</sup> *Ibid.*, 558; *A.*, ii, 896.

detect less than 0.05 milligram of arsenious oxide in this way.<sup>43</sup> W. van Ryn<sup>44</sup> points out that sodium fluoride may prevent completely the formation of arsenical mirrors in the Marsh-Berzelius method, although it has no influence on the Gutzeit or Flückiger reaction. E. Salkowski<sup>45</sup> deals with the detection and estimation of arsenic in urine. To detect arsenic in sulphur, J. Brand<sup>46</sup> extracts the finely-powdered sulphur with ammonia.

M. Orthey<sup>47</sup> has made a careful study of certain volumetric methods of estimating manganese in ferro-manganese ores, and he shows that the Volhard-Wolff method<sup>48</sup> and those of von Knorre<sup>49</sup> and Blair<sup>50</sup> give results agreeing well with those yielded by the ordinary gravimetric method; the first two are specially recommended.<sup>51</sup> For the detection and colorimetric estimation of manganese, M. Duyk<sup>52</sup> makes use of the red coloration produced when a trace of manganese is heated with an alkaline solution of hypochlorite in presence of a trace of copper sulphate. H. W. Rowell<sup>53</sup> estimates small quantities of bismuth colorimetrically as iodide.

Miss Z. Kahan<sup>54</sup> has devised a method for the quantitative separation of barium and strontium. O. Hauser, in conjunction with F. Wirth, has published some important data on the solubility of the oxalates of the rare earths in dilute sulphuric and oxalic acids.<sup>55</sup> Later<sup>56</sup> he shows that the precipitation of these oxalates is incomplete in presence of uranyl salts. M. Dittrich<sup>57</sup> describes the separation of cerium from other metals and its estimation.

To separate lithium from other alkali metals, L. Kahlenberg and F. C. Krauskopf<sup>58</sup> take advantage of the solubility of lithium chloride in pyridine. The precipitation of potassium as cobalti-

<sup>43</sup> For microchemical reactions of arsenic, see also G. Denigès, *Compt. rend.*, 1908, **147**, 596, 744; *A.*, ii, 1070.

<sup>44</sup> *Pharm. Weekblad.*, 1908, **45**, 98; *A.*, ii, 224.

<sup>45</sup> *Zeitsch. physiol. Chem.*, 1908, **56**, 95; *A.*, ii, 734.

<sup>46</sup> *Zeitsch. ges. Brauwesen*, 1908, **31**, 33; *A.*, ii, 532.

<sup>47</sup> *Zeitsch. anal. Chem.*, 1908, **47**, 547; *A.*, ii, 898.

<sup>48</sup> *Ibid.*, 1880, **20**, 271; compare Volhard, *A.*, 1880, 141.

<sup>49</sup> *Ibid.*, 1904, **43**, 643; compare *A.*, 1902, ii, 108.

<sup>50</sup> *Ibid.*, 1904, **43**, 647; compare *A.*, 1904, ii, 683.

<sup>51</sup> Compare E. W. Meyer, *Zeitsch. angew. Chem.*, 1907, **20**, 1980; *A.*, ii, 71; L. Sacerdoti, *L'Industria Chimica*, 1907, **7**, 258; *A.*, ii, 228.

<sup>52</sup> *Ann. Chim. anal.*, 1907, **12**, 465; *A.*, ii, 70.

<sup>53</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 102; *A.*, ii, 325.

<sup>54</sup> *Analyst*, 1908, **33**, 12; *A.*, ii, 133.

<sup>55</sup> *Zeitsch. anal. Chem.*, 1908, **47**, 389; *A.*, ii, 778.

<sup>56</sup> *Ibid.*, 677; *A.*, ii, 987.

<sup>57</sup> *Ber.*, 1908, **41**, 4373.

<sup>58</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 1104; *A.*, ii, 777.

nitrite " is dealt with by W. A. Drushel,<sup>60</sup> and by W. Auermeth,<sup>61</sup> who shows that the precipitate obtained with de Koninck's cobalt reagent is not of constant composition.

For the estimation of tungsten and its separation from other substances, advantage may be taken of the fact that it is volatilised as oxychlorides when heated strongly in a mixture of chlorine and sulphur chloride,<sup>62</sup> or when heated at 500° in a current of air charged with chlorine.<sup>63</sup> Tungsten trioxide is reduced by hydrogen at 600—900°, and may be then volatilised by treatment with chlorine.<sup>64</sup> G. von Knorre has applied his benzidine method<sup>65</sup> to the estimation of tungsten in steel containing chromium.<sup>66</sup> F. W. Hinrichsen and L. Wolter<sup>67</sup> state that the results are low. They describe other methods of estimating both tungsten and chromium. Methods for the estimation of vanadium in presence or absence of iron are described by T. Warynski and B. Mdivani,<sup>68</sup> and by G. Edgar.<sup>69</sup>

*Electrochemical Analysis.*—The work conducted in this department during the year indicates steady progress, and shows the increasing utility of electrolytic methods. F. Foerster<sup>70</sup> summarises our knowledge of rapid electrolytic methods, especially those in which rotating electrodes are employed. His claim of priority for rotating electrodes has been disputed by A. Clässon,<sup>71</sup> and a series of polemical papers by these authors have followed.<sup>72</sup> F. M. Perkin<sup>73</sup> remarks that rotating electrodes were first described by Gooch and Medway, E. Smith, and himself almost simultaneously. F. A. Gooch and F. B. Beyer<sup>74</sup> employ as cathode a Gooch crucible with asbestos filter in the case of precipitates which do not adhere firmly.

The reduction of alkali nitrate to ammonia in presence of copper was studied by Easton in 1904, and subsequently by Ingham in 1905. O. L. Shinn<sup>75</sup> states that in order to realise Ingham's

<sup>59</sup> Adie and Wood, *Trans.*, 1900, **77**, 1076.

<sup>60</sup> *Zeitsch. anorg. Chem.*, 1907, **56**, 223; 1898, **59**, 97; *A.*, ii, 66, 735.

<sup>61</sup> *Centr. Min.*, 1908, 513; *A.*, ii, 897.

<sup>62</sup> F. Bouillon, *Compt. rend.*, 1908, **146**, 1102; *A.*, ii, 737.

<sup>63</sup> P. Nicolardot, *ibid.*, **147**, 795; *A.*, ii, 1074.

<sup>64</sup> E. Defacqz, *ibid.*, **146**, 1319; *A.*, ii, 737.

<sup>65</sup> *Ann. Report*, 1905, 192.

<sup>66</sup> *Zeitsch. anal. Chem.*, 1908, **47**, 337; *A.*, ii, 779.

<sup>67</sup> *Zeitsch. anorg. Chem.*, 1908, **59**, 183; *A.*, ii, 900.

<sup>68</sup> *Ann. Chem. anal.*, 1908, **13**, 209, 210; *A.*, ii, 636, 736.

<sup>69</sup> *Amer. J. Sci.*, 1908, [iv], **26**, 79; *A.*, ii, 736.

<sup>70</sup> *Zeitsch. Elektrochem.*, 1908, **14**, 3.

<sup>71</sup> *Ibid.*, 90.

<sup>72</sup> *Ibid.*, 141, 208, 239; *A.*, ii, 432, 529.

<sup>73</sup> *Ibid.*, 143; *A.*, ii, 432.

<sup>74</sup> *Amer. J. Sci.*, 1908, **25**, 249; *A.*, ii, 529.

<sup>75</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 1378; *A.*, ii, 893.



results, the anode must be rotated slowly; the current should be 4—5 amperes at 10 volts, and not more than 20—25 c.c. of  $N/5$ -sulphuric acid should be present. He also finds that it is sometimes necessary to add a second or even a third quantity of copper sulphate in order to complete the reduction.

H. W. Gillett<sup>76</sup> describes the conditions necessary for the deposition of silver in presence of copper from ammoniacal tartrate solutions, an important point is that when the electrolysis is carried out at a temperature below 20° very rapid rotation of the anode is necessary. Miss M. E. Holmes<sup>77</sup> deals with the separation of cadmium from a large number of metals. O. Scheen<sup>78</sup> gives some details for the electrolytic estimation of antimony. In conjunction with his paper should be read that of E. Cohen.<sup>79</sup> H. J. S. Sand has continued his useful studies on the rapid separation of metals,<sup>80</sup> and in a second communication<sup>81</sup> it is shown that by means of the apparatus previously described with rotating anodes, coherent deposits of antimony may be obtained from solutions in sulphuric acid (1: 1) in the presence of hydrazine sulphate; the temperature must be kept above 100° with a cathode potential measured against an auxiliary 2*N*-sulphuric acid of 0.65 volt. Tin is not deposited unless the auxiliary potential rises above 0.8 volt. In order to effect its deposition after separating the antimony, oxalic acid is added, the solution neutralised with ammonia, and again acidified with sulphuric acid. Considering the difficulty of this separation on theoretical grounds, the results are extremely good. For the separation of copper from iron, an apparatus is described, including a parchment paper diaphragm. The influence of temperature on the estimation of copper is discussed by J. R. Withrow,<sup>82</sup> whilst E. E. Free<sup>83</sup> deals with the estimation of small quantities of copper. A. Thiel<sup>84</sup> shows that nickel can be estimated accurately by the electrolysis of the nitrate provided no nitrite be present, sufficient excess of ammonia be added, and a straight wire of passive iron used as anode (platinum anodes are attacked); he gives conditions for the separation of nickel and copper quantitatively. F. Foerster and W. Treadwell<sup>85</sup> confirm Thiel and Windel-

<sup>76</sup> *J. Physical Chem.*, 1908, 12, 26; *A.*, ii, 226.

<sup>77</sup> *J. Amer. Chem. Soc.*, 1908, 30, 1865.

<sup>78</sup> *Zeitsch. Elektrochem.*, 1908, 14, 257; *A.*, ii, 636.

<sup>79</sup> *Ibid.*, 301; *A.*, ii, 636.

<sup>80</sup> *Ann. Report*, 1907, 207.

<sup>81</sup> *Trans.*, 1908, 93, 1572.

<sup>82</sup> *J. Amer. Chem. Soc.*, 1908, 30, 381; *A.*, ii, 432.

<sup>83</sup> *J. Physical Chem.*, 1908, 12, 28; *A.*, ii, 227.

<sup>84</sup> *Zeitsch. Elektrochem.*, 1908, 14, 201; *A.*, ii, 538.

<sup>85</sup> *Ibid.*, 89; *A.*, ii, 324.

Schmidt's statement,<sup>86</sup> that in separating nickel from zinc by electrolysis an ammoniacal solution containing sodium sulphide as electrolyte, the deposited nickel contains sulphur. As pointed out by A. Fischer, however,<sup>87</sup> without sodium sulphate a much higher current density is required. He gives conditions for the estimation of the two metals. It would appear advisable, taking into account the observations of the various authors, to dissolve the nickel first deposited and again electrolyse. In the electrolytic estimation of nickel, A. Schumann shows<sup>88</sup> that a gauze cathode is preferable to a disk or cone cathode. R. Goldschmidt,<sup>89</sup> in the electrolysis of zinc silicofluoride, uses a stationary slanting anode, over which the solution passes and is returned by a pump. F. J. Metzger and H. T. Beans' method of estimating bismuth by electrolysis an acetic acid solution seems to be very accurate on the evidence given.<sup>90</sup> J. Peset,<sup>91</sup> after electrolysis a bismuth salt, adds a known weight of cadmium sulphate, and continues the electrolysis. The deposited cadmium is said to protect the bismuth from oxidation and to render it more adherent.

G. Gallo and G. Cenni<sup>92</sup> state that by electrolysis a solution of thallium sulphate, faintly acidified with oxalic acid, at the ordinary temperature in a Classen's capsule with a rotating platinum cathode, the whole of the thallium is deposited at the anode apparently as a new oxide,  $Tl_2O_5$ .

J. S. Goldbaum and E. F. Smith<sup>93</sup> have continued their experiments on the separation of the alkali metals<sup>94</sup> to the chlorides of ammonium, caesium, rubidium, and lithium with satisfactory results; attempts to separate potassium and ammonium were unsuccessful.

*General.*—Sir W. Crookes<sup>95</sup> points out the utility of iridium crucibles in analysis, chiefly on account of the high resistance of the metal against the attack of reagents; but he states that rhodium possesses almost the same resistance, and its cost would be less because of its lower density. It is interesting to note that fused silica apparatus, which is adapted for so many purposes in analysis, has recently been considerably cheapened.

<sup>86</sup> *Zeitsch. angew. Chem.*, 1907, 20, 1137; compare *A.*, 1907, ii, 601.

<sup>87</sup> *Chem. Zeit.*, 1908, 32, 185; *A.*, ii, 324.

<sup>88</sup> *Zeitsch. angew. Chem.*, 1908, 21, 2579; *A.*, 1909, ii, 97.

<sup>89</sup> *Bull. Soc. chim. Belg.*, 1908, 22, 138; *A.*, ii, 536.

<sup>90</sup> *J. Amer. Chem. Soc.*, 1908, 30, 539; *A.*, ii, 541.

<sup>91</sup> *Zeitsch. anal. Chem.*, 1908, 47, 401; *A.*, ii, 780.

<sup>92</sup> *Atti R. Acad. Lincei*, 1908, [v], 17, ii, 276; *A.*, ii, 986.

<sup>93</sup> *J. Amer. Chem. Soc.*, 1908, 30, 1705; *A.*, ii, 1072.

<sup>94</sup> *Ibid.*, 1907, 29, 447, 1445, 1455; *A.*, 1907, ii, 574, 988.

<sup>95</sup> *Proc. Roy. Soc.*, 1908, 80, A., 535; *A.*, ii, 702.

A modification of the Ostwald pipette for calibrating burettes and other measuring vessels has been devised by O. von Spindler.<sup>96</sup> Other useful apparatus in connexion with volumetric analysis is described by G. Müller<sup>97</sup> and G. Muller and O. Berchem.<sup>98</sup> A. Gawalowski<sup>99</sup> has devised an apparatus for mixing liquids during a reaction. A simple manometer for use when distilling under diminished pressure is described by N. L. Gebhard,<sup>1</sup> and H. Süchting<sup>2</sup> has devised an automatic stirring arrangement which can be applied to liquids liable to bump when being distilled under diminished pressure. P. A. Kober<sup>3</sup> describes an apparatus whereby Folin's method may be applied to Kjeldahl nitrogen determinations; and, later,<sup>4</sup> he deals with the estimation of carbamide by Folin's method. A new form of pycnometer for very accurate work has been devised by W. R. Bousfield.<sup>5</sup>

*Gas Analysis.*—Useful methods for the detection of ozone, hydrogen peroxide, and nitrogen peroxide in air are described by E. H. Keiser and L. McMaster.<sup>6</sup> P. Ménière<sup>7</sup> gives a method for the estimation of mercury vapour in air, whilst J. Ogier and E. Kohn-Abrest<sup>8</sup> deal with the detection and estimation of small quantities of carbon monoxide in air. C. A. Keane and H. Burrows<sup>9</sup> show that the autolysator for the automatic determination of carbon dioxide in furnace gases gives accurate results. A. Fraenckel<sup>10</sup> deals with the estimation of phosphorus, sulphur, and silica in acetylene. W. A. Bone and R. V. Wheeler<sup>11</sup> describe an apparatus for the analysis of mixtures of hydrocarbon gases, and A. E. Hill<sup>12</sup> describes a new gas burette. A. Stock<sup>13</sup> deals with the uses of the mercury trough in the manipulation of gases and their treatment with reagents. He gives some useful hints on the re-purification of mercury. New gas analysis apparatus has

<sup>96</sup> *Schweiz. Woch. Chem. Pharm.*, 1908, **46**, 145; *A.*, ii, 625.

<sup>97</sup> *Chem. Zeit.*, 1908, **44**, 532; *A.*, ii, 626.

<sup>98</sup> *Ibid.*, 711; *A.*, ii, 775.

<sup>99</sup> *Zetsch. anal. Chem.*, 1908, **47**, 697; *A.*, ii, 939.

<sup>1</sup> *Proc.*, 1908, **24**, 51.

<sup>2</sup> *Zetsch. anal. Chem.*, 1908, **47**, 755; *A.*, 1909, ii, 35.

<sup>3</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 1131; *A.*, ii, 626.

<sup>4</sup> *Ibid.*, 1279; *A.*, ii, 893.

<sup>5</sup> *Trans.*, 1908, **93**, 679.

<sup>6</sup> *Amer. Chem. J.*, 1908, **39**, 96; *A.*, ii, 222.

<sup>7</sup> *Compt. rend.*, 1908, **146**, 754; *A.*, ii, 433.

<sup>8</sup> *Ann. Chim. anal.*, 1908, **13**, 169, 218; *A.*, ii, 631, 632.

<sup>9</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 608; *A.*, ii, 735.

<sup>10</sup> *J. Gasbeleucht.*, 1908, **51**, 431; *A.*, ii, 983.

<sup>11</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 10; *A.*, ii, 221.

<sup>12</sup> *Trans.*, 1908, **93**, 1857.

<sup>13</sup> *Ber.*, 1908, **41**, 3834; *A.*, 1909, ii, 89.

been devised by R. Ross and J. P. Leather.<sup>14</sup> H. Franzen<sup>15</sup> has devised a simple apparatus by means of which a gas may be absorbed from a mixture containing a large proportion of non-absorbable gas. L. M. Dennis and E. S. McCarthy<sup>16</sup> recommend an ammoniacal solution of nickel cyanide as an absorbent for benzene in illuminating gas.

*Water Analysis.*—F. Telle<sup>17</sup> proposes a solution containing 0.344 gram of gypsum per litre as a standard in the Clark process. The method suggested by C. J. Blacher and J. Jacoby,<sup>18</sup> of estimating alkaline earths by titration with potassium stearate and phenolphthalein, is worthy of attention. H. Noll<sup>19</sup> gives a method for the estimation of carbonic acid and carbonates in chalybeate waters. E. Ernyei<sup>20</sup> describes a method of estimating manganese in waters. A useful paper on the systematic investigation of potable waters is that by G. Romyn,<sup>21</sup> who discusses the flora and fauna of potable waters.<sup>22</sup> J. E. Purvis and R. M. Courtauld<sup>23</sup> show that organic nitrogen compounds are attacked to a certain extent by the copper-zinc couple, so that the estimation of nitrates and nitrites by this method in presence of organic nitrogen compounds gives too high results. A simple apparatus for observing the rate of absorption of oxygen by polluted waters has been devised by W. E. Adeney.<sup>24</sup> K. Saito<sup>25</sup> points out that *Bacillus coli communis* is so widely disseminated that great caution must be exercised in condemning a water as polluted because of its presence.

G. O. Adams and A. W. Kimball<sup>26</sup> show that, in the estimation of nitrogen in sewage by the Kjeldahl method, the ammonia formed may be nesslerised. H. W. Clark and G. O. Adams<sup>27</sup> state that the odour and appearance of incubated effluents give a better idea of their putrescibility than does the measurement of the time required to decolorise dyes.

<sup>14</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 491; *A.*, ii, 626.

<sup>15</sup> *Zeitsch. anorg. Chem.*, 1908, **57**, 395; *A.*, ii, 425.

<sup>16</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 233; *A.*, ii, 435.

<sup>17</sup> *J. Pharm. Chim.*, 1908, [vi], **27**, 380; *A.*, ii, 535.

<sup>18</sup> *Chem. Zeit.*, 1908, **32**, 744; *A.*, ii, 897.

<sup>19</sup> *Zeitsch. angew. Chem.*, 1908, **21**, 640, 1455; G. Lunge, *ibid.*, 833; *A.*, ii, 435.

<sup>20</sup> *Chem. Zeit.*, 1908, **32**, 41; *A.*, ii, 133.

<sup>21</sup> *Pharm. Weekblad*, 1908, **45**, 402.

<sup>22</sup> *Chem. Weekblad. Beilage*, 1908, 30/5; *Pharm. Weekblad*, 1908, **45**, 1287.

<sup>23</sup> *Proc. Camb. Phil. Soc.*, 1908, **14**, 441; *A.*, ii, 776.

<sup>24</sup> *Sci. Proc. Roy. Dubl. Soc.*, 1908, **11**, 280; *A.*, ii, 781.

<sup>25</sup> *Arch. Hygiene*, 1908, **63**, 215.

<sup>26</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 1034.

<sup>27</sup> *Ibid.*, 1037.

*Organic Chemistry.*

*Qualitative.*—This portion of the literature is as voluminous as usual, but it will only be necessary to mention a few papers. L. E. Hinkel<sup>28</sup> deals with the detection of methyl alcohol in ethyl alcohol. I. Lifschütz<sup>29</sup> states that the green colour produced by warming an acetic acid solution of cholesterol with benzoyl peroxide, although less sensitive than Liebermann's reaction, has advantages in the position of the absorption bands. Some colour reactions of cholesterol and onycholesterol are described by L. Golodetz,<sup>30</sup> and, by the same author,<sup>31</sup> a colour reaction with formaldehyde and benzoyl peroxide. In connexion with Hehner's test for formaldehyde in milk,<sup>32</sup> H. D. Dakin<sup>33</sup> characterises a number of aliphatic ketones and aldehydes by the appearances and melting points of their *p*-nitrophenylhydrazones. H. J. H. Fenton and G. Barr<sup>34</sup> tabulate the colour reactions produced by formic, oxalic, dihydroxy-tartaric, pyruvic,  $\alpha\alpha$ -dimethylglutaric, lactic, saccharic, lævulic, and oxalacetic acids when treated with resorcinol, phenol, pyrogallol, or *o*-cresol in presence of concentrated sulphuric acid. According to W. M. Dehn and S. F. Scott,<sup>35</sup> sodium hypobromite gives characteristic colours with phenols and aromatic amines. T. Silbermann and N. Ozorovitz<sup>36</sup> make use of the formation of resinous condensation products (insoluble in ordinary solvents) from formaldehyde and dihydric phenols to detect and identify the latter. F. A. Steensma's observations,<sup>37</sup> that an aromatic or heterocyclic aldehyde in presence of a mineral acid gives a colour with phenols or with heterocyclic compounds containing the group C:CH, are most interesting as showing that certain colour reactions can actually be predicted, a generalisation of which he cites specific instances. The formation of an additive (red) compound with *p*-dimethylaminobenzaldehyde is recommended by B. von Pawlewski<sup>38</sup> as a characteristic reaction of anthranilic acid. Some new differential reactions of the naphthols are described by Volcy-Boucher.<sup>39</sup> C. Lefebvre<sup>40</sup> describes some biochemical reactions

<sup>28</sup> *Analyst*, 1908, **33**, 417; *A.*, ii, 1076. <sup>29</sup> *Ber.*, 1908, **41**, 252; *A.*, ii, 233.

<sup>30</sup> *Chem. Zeit.*, 1908, **32**, 160; *A.*, ii, 328. <sup>31</sup> *Ibid.*, 245; *A.*, ii, 330.

<sup>32</sup> See F. von Fillinger, *Zeitsch. Nahr. Genussm.*, 1908, **16**, 226; *A.*, ii, 902.

<sup>33</sup> *J. Biol. Chem.*, 1908, **4**, 235; *A.*, ii, 234.

<sup>34</sup> *Proc. Camb. Phil. Soc.*, 1908, **14**, 386; *A.*, ii, 438.

<sup>35</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 1418; *A.*, i, 780.

<sup>36</sup> *Bul. Soc. Sci. Bucuresci*, 1908, **17**, 41; *A.*, 1909, ii, 98.

<sup>37</sup> *Biöchem. Zeitsch.*, 1908, **8**, 203; *A.*, ii, 442.

<sup>38</sup> *Ber.*, 1908, **41**, 2353; *A.*, i, 638.

<sup>39</sup> *Ann. Chim. anal.*, 1908, **13**, 335; *A.*, ii, 990.

<sup>40</sup> *Arch. Pharm.*, 1907, **245**, 493; *A.*, ii, 57.

(enzymic) for the detection of sugars and glucosides in the *Taxaceæ*. B. Tollens and F. Rorive<sup>41</sup> describe colour and spectral reactions of sugars and their derivatives on treatment with naphtharesorcinol. B. Tollens<sup>42</sup> uses the same reagent for the detection of glycuronic acid in urine.<sup>43</sup> E. C. Kendall and H. C. Sherman<sup>44</sup> recommend *p*-bromobenzylhydrazide as a reagent for the detection and identification of various sugars; the hydrazone obtained from galactose is insoluble in boiling alcohol, whilst those of mannose and lævulose are sparingly, and that of dextrose readily, soluble. It is well known that even the hexoses give traces of furfuraldehyde when boiled with acids. C. Fleig<sup>45</sup> shows that furfuraldehyde gives colorations with indole and with carbazole. L. Garnier<sup>46</sup> deals with some colour reactions of digitalis glucosides.

In connexion with alkaloids, C. Reichard<sup>47</sup> describes some reactions of tropacocaine, which serve to differentiate it from cocaine. G. Denigès<sup>48</sup> gives some reactions of hordenine, and L. Krauss<sup>49</sup> some reactions of synthetic suprarenine.

F. Schulz<sup>50</sup> calls attention to the red coloration given when a solution of (crude, not pure) picric acid in benzene is added to a mineral oil, a reaction which serves for the detection of the latter in animal and vegetable oils. Tests for oleic acid are described by A. Manea<sup>51</sup> and I. Lifschütz.<sup>52</sup>

*Quantitative.*—There are a few papers dealing with elementary analysis demanding notice. M. Dennstedt<sup>53</sup> details the precautions to be taken in his simplified method of determining carbon in difficultly combustible substances.<sup>54</sup> He describes<sup>55</sup> a new form of soda-lime absorption apparatus, and A. E. Hill<sup>56</sup> a new form of potash bulbs. W. Lenz<sup>57</sup> points out that the percentage of carbon

<sup>41</sup> *Ber.*, 1908, **41**, 1783; *A.*, ii, 638.

<sup>42</sup> *Ibid.*, 1788; *A.*, ii, 639.

<sup>43</sup> See also K. Tollens, *Zeitsch. physiol. Chem.*, 1908, **56**, 115; *A.*, ii, 740; and compare J. A. Mandel and C. Neuberg, *Biochem. Zeitsch.*, 1908, **13**, 148; *A.*, ii, 993.

<sup>44</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 145; *A.*, ii, 902.

<sup>45</sup> *J. Pharm. Chem.*, 1908, [iv], **28**, 385; *A.*, ii, 1077.

<sup>46</sup> *Ibid.*, **27**, 369; *A.*, ii, 544.

<sup>47</sup> *Pharm. Zentr.-h.*, 1908, **49**, 337; *A.*, ii, 643.

<sup>48</sup> *Bull. Soc. chim.*, 1908, [iv], **3**, 736; *A.*, i, 735.

<sup>49</sup> *Apoth. Zeit.*, 1908, **23**, 701.

<sup>50</sup> *Bull. Soc. Sci., Bucuresci*, 1908, **17**, 256.

<sup>50</sup> *Chem. Zeit.*, 1908, **32**, 345.

<sup>52</sup> *Zeitsch. physiol. Chem.*, 1908, **56**, 446; *A.*, i, 754.

<sup>53</sup> *Ber.*, 1908, **41**, 60; *A.*, ii, 321.

<sup>54</sup> Compare J. Zaleski, *Bull. Acad. Sci. Cracow.*, 1907, ii, 646; *A.*, ii, 132.

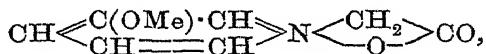
<sup>55</sup> *Chem. Zeit.*, 1908, **32**, 77; *A.*, ii, 225.

<sup>56</sup> *Proc.*, 1908, **24**, 182.

<sup>57</sup> *Zeitsch. anal. Chem.*, 1907, **46**, 557; *A.*, ii, 65.

obtained by the Carrasco-Plancher method<sup>58</sup> is apt to be low on account of the formation of carbon monoxide. O. Carrasco and E. Belloni<sup>59</sup> recommend a modification of the method, in which the organic substance is mixed with powdered platinised biscuit porcelain as catalyst instead of cupric oxide. M. Dennstedt and F. Hassler<sup>60</sup> describe a method and apparatus for the simultaneous estimation of carbon, hydrogen, halogen, and nitrogen, and from the one example given—analysis of pyridine platinochloride—the results would appear to be accurate enough for purposes of check.<sup>61</sup> For the estimation of the halogens and sulphur, W. Parr shows that his method of heating with sodium peroxide and "boromagnesium" mixture (see p. 186) may be used. To estimate sulphur in indiarubber, he burns the sample with sodium peroxide, potassium chlorate, and benzoic acid.<sup>62</sup> According to H. D. Richmond,<sup>63</sup> the higher results obtained when the nitrogen in casein is estimated by Dumas's method, as compared with Kjeldahl's method, is due to the presence of unburnt carbon monoxide in the former case. He also describes a simple method of estimating nitrogen in compounds containing the triazo-group. A series of papers have been published by P. Blackman<sup>64</sup> on a new method of estimating vapour density.

J. Herzog and V. H. Hâncu<sup>65</sup> show that the number of hydroxyl groups present in a phenol may be determined by condensing it with diphenylcarbonyl chloride, hydrolysing the resulting urethane, and weighing the diphenylamine formed. A. Kirpal<sup>66</sup> points out that methoxyl determinations in such a substance as



either by the Zeisel or by the Herzig-Meyer method are invariably low, probably due to the wandering of the methyl group from the oxygen to the nitrogen atom.<sup>67</sup>

G. T. Morgan and T. Cook<sup>68</sup> describe a useful distillation flask adapted for use in many methods for the analysis of organic sub-

<sup>58</sup> *Ann. Report*, 1906, 211.

<sup>59</sup> *J. Pharm. Chim.*, 1908, [vi], 27, 469; *A.*, ii, 631.

<sup>60</sup> *Ber.*, 1908, 41, 2778; *A.*, ii, 984.

<sup>61</sup> Compare J. Lehenter, *Programm d. Oberrealschule. Innsbruck*, 1908; *Chem. Zentr.*, 1908, ii, 635.

<sup>62</sup> See p. 186.

<sup>63</sup> *Analyst*, 1908, 33, 179; *A.*, ii, 530.

<sup>64</sup> *Ber.*, 1908, 41, 768, 881, 1588, 2487, 4141; compare *Proc.*, 1908, 24, 8; *A.*, ii, 157, 564; *A.*, 1909, ii, 21.

<sup>65</sup> *Ber.*, 1908, 41, 638; *A.*, ii, 327.

<sup>66</sup> *Ibid.*, 819; *A.*, ii, 436.

<sup>67</sup> Compare J. Herzig, *Monatsh.*, 1908, 29, 295; *A.*, ii, 638.

<sup>68</sup> *Analyst*, 1908, 33, 118; *A.*, ii, 424.

stances in which distillation is necessary. R. Corradi<sup>69</sup> recommends the gasometric (hypobromite) method of determining the ammonia formed in the Kjeldahl method. V. von Cordier<sup>70</sup> describes a modification of Hufner's hypobromite method for the estimation of nitrogen, and a special apparatus for carrying it out.

H. Bollenbach<sup>71</sup> has modified de Haën's volumetric process of estimating ferrocyanides, and the evidence he brings forward shows that the results are trustworthy. A valuable paper on the analysis of commercial ferrocyanides is that by H. G. Colman.<sup>72</sup> The paper deals with the direct estimation of the ferrocyanide by titration with copper or zinc sulphate, the estimation of the iron and the calculation of the ferrocyanide from the results, and the estimation of the hydrogen cyanide. G. Heikel<sup>73</sup> has published a useful paper on the limits of accuracy of the Messinger and Denigès' methods of estimating acetone. V. F. Herr<sup>74</sup> describes a new dephlegmator for the fractionation of naphtha. I. Bay<sup>75</sup> shows that carbon disulphide may be estimated in benzene by precipitating with phenylhydrazine, and weighing the resulting phenylhydrazine phenylthiocarbazate,  $\text{CS}_2(\text{Ph}\cdot\text{NH}\cdot\text{NH}_2)_2$ , dried in a vacuum desiccator. This process is, however, not new; it is commonly used, and was first described by Liebermann and Seycwetz.<sup>76</sup> According to F. Utz,<sup>77</sup> when picric acid is heated with sodium hydroxide and hydrogen peroxide, the whole of the nitrogen is obtained as nitrate, and may be estimated by the "nitron" method, whilst M. Busch and G. Blume<sup>78</sup> show that picric acid may be estimated by weighing it as "nitron" picrate; halides and their oxygenated salts, nitrates, nitrites, and chromates must be absent. F. Raschig<sup>79</sup> gives a method for estimating *m*-cresol in presence of the *o*- and *p*-isomerides; it is adversely criticised by J. Herzog.<sup>80</sup>

The methods of estimating starch in cereals, which depend on determining the reducing power after hydrolysis with either diastase or acid, or with both successively, are lengthy and inaccurate, since reducing sugars other than those originating from the starch are invariably present among the products of hydrolysis. Although

<sup>69</sup> *Boll. chim. farm.*, 1907, **46**, 861; *A.*, ii, 130.

<sup>70</sup> *Zeitsch. anal. Chem.*, 1908, **47**, 682; *A.*, ii, 983.

<sup>71</sup> *Ibid.*, 687; *A.*, ii, 996.

<sup>72</sup> *Analyst*, 1908, **33**, 261.

<sup>73</sup> *Chem. Zeit.*, 1908, **32**, 75; *A.*, ii, 235.

<sup>74</sup> *Ibid.*, 148; *A.*, ii, 232.

<sup>75</sup> *Compt. rend.*, 1908, **146**, 132; *A.*, ii, 226.

<sup>76</sup> *Ber.*, 1891, **24**, 788; *A.*, 1891, 681.

<sup>77</sup> *Zeitsch. anal. Chem.*, 1908, **47**, 110; *A.*, ii, 233.

<sup>78</sup> *Zeitsch. angew. Chem.*, 1908, **21**, 354; *A.*, ii, 328.

<sup>79</sup> *Pharm. Zeit.*, 1908, **53**, 99; *A.*, ii, 233.

<sup>80</sup> *Ibid.*, 141; *A.*, ii, 233.



no known method gives anything but approximate accuracy, in the writer's hands the most satisfactory and rapid method is the Dubrunfaut-Effront, which consists in triturating the ground cereal with concentrated hydrochloric acid and polarising the soluble starch. Last year C. J. Lintner<sup>81</sup> proposed a modification of this method, and later O. Wenglein<sup>82</sup> suggested the use of sulphuric acid (D 1.7) instead of hydrochloric, under which conditions the rotatory power of barley starch is found to be  $[\alpha]_D 191.7^\circ$ . Lintner has confirmed Wenglein's results,<sup>83</sup> and adopts his suggestions. E. Ewers<sup>84</sup> points out that substances other than starch are dissolved, and that the results are thereby vitiated. He proposes modifications, his latest suggestion<sup>85</sup> being treatment with one per cent. hydrochloric acid at  $100^\circ$ , and clarification with ammonium molybdate, before polarising. In connexion with sugars, Barfoed's copper acetate solution was put forward as one which was not reduced by maltose and lactose, and F. C. Hinkel and H. C. Sherman<sup>86</sup> have determined the conditions under which in a mixture of dextrose and the reducing bioses mentioned, only the former exhibits reducing power. F. Watts and H. A. Tempany<sup>87</sup> recommend the use of dry basic lead acetate for clarifying commercial sugar solutions. H. C. Prinsen Geerligs<sup>88</sup> points out that the error due to the precipitation of laevulose only occurs in the case of commercial samples containing impurities precipitable by the lead reagent, whilst O. Schrefeld<sup>89</sup> states that this source of error is to be avoided by the employment of neutral lead acetate. F. Watts and H. A. Tempany<sup>90</sup> recommend the Fehling-Violette solution as the least liable to auto-reduction. In the estimation of invert-sugar in presence of sucrose, they find that one gram of the latter exerts a reducing power equal to 0.0033 gram of invert-sugar. The writer and T. Rendle<sup>91</sup> find that sucrose has no influence on the estimation of invert-sugar until its amount exceeds 30 per cent. of the total sugars; with a mixture of equal parts of the sugar, the invert-sugar would be over-estimated by 0.8 per cent., whilst when the invert-sugar only represents one per cent. of the mixture, the

<sup>81</sup> *Zeitsch. ges. Brauwesen*, 1907, **30**, 109; compare *A.*, 1907, ii, 823.

<sup>82</sup> *Ibid.*, 1908, **31**, 53.

<sup>83</sup> *Zeitsch. Nahr. Genussm.*, 1908, **16**, 509; *A.*, ii, 1077.

<sup>84</sup> *Zeitsch. öffentl. Chem.*, 1908, **14**, 150; *A.*, ii, 543.

<sup>85</sup> *Chem. Zeit.*, 1908, **32**, 996.

<sup>86</sup> *J. Amer. Chem. Soc.*, 1907, **29**, 1744; *A.*, ii, 235.

<sup>87</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 53; *A.*, ii, 236.

<sup>88</sup> *Intern. Sugar J.*, 1908, **10**, 500; *A.*, ii, 990.

<sup>89</sup> *Zeitsch. Ver. deut. Zuckerind.*, 1908, 947; *A.*, ii, 1076.

<sup>90</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 191; *A.*, ii, 437.

<sup>91</sup> *Analyst*, 1908, **33**, 167; *A.*, ii, 542.

amount returned may be 14 per cent. too much. These results confirm those of Watts and Tempary,<sup>92</sup> who, however, dealt only with high proportions of sucrose to invert-sugar. The writer and G. C. Jones<sup>93</sup> have shown that the volumetric method of estimating reducing sugars, using ferrous thiocyanate as indicator, gives results quite as accurate as the gravimetric method, and is far more rapid. The writer would point out, however, that with commercial products, such as molasses containing iron, the ferrous thiocyanate indicator cannot be used. It is well known that the rotatory power of levulose decreases as the temperature is raised, and that at 87° it is equal but opposite in sign to that of dextrose, so that equal amounts of dextrose and levulose are optically inactive at 87°. For the analysis of commercial invert-sugar, the measurement of the change or rotatory power with rise of temperature is useful, and the apparatus described by A. P. Sy<sup>94</sup> for making polarimetric determinations at high temperatures is much to be appreciated.

T. W. Harrison and F. M. Perkin<sup>95</sup> find that the Valenta method is untrustworthy for the estimation of tar oils in admixture with mineral oils, the latter being not absolutely insoluble in methyl sulphate.<sup>96</sup> W. H. Emerson<sup>97</sup> has redetermined the solubility of stearic acid in alcohol at 0° for the purpose of the Hehner-Mitchell method. R. K. Dons<sup>98</sup> describes a modification of his method of determining the caprylic acid value in butter fat. J. Lewkowitsch<sup>99</sup> gives constants of, and other information on, carapa oil; and<sup>1</sup> he publishes constants of ochoco fat from the seeds of one of the Myristicaceæ. M. Tsujimoto<sup>2</sup> gives some constants of Japanese tea oil. Such processes of determining unsaturated fats as those of Hübl and Wys (iodine absorption) are often used as mere empirical tests; the scientific principle underlying them is brought out, however, by S. Fokin's experiments,<sup>3</sup> showing that the same results may be obtained by determining the hydrogen value (c.c. of hydrogen at 0° and 760 mm. absorbed by one gram of the substance).<sup>4</sup> H. Matthes and O. Rohdich,<sup>5</sup> working on 13 kilos. of

<sup>92</sup> *Loc. cit.* <sup>93</sup> *Analyst*, 1908, **33**, 160; *A.*, ii, 541.

<sup>94</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 1790; *A.*, ii, 1076.

<sup>95</sup> *Analyst*, 1908, **33**, 2; *A.*, ii, 135.

<sup>96</sup> Compare Graeffe, *Ann. Report*, 1907, 211.

<sup>97</sup> *J. Amer. Chem. Soc.*, 1907, **29**, 1750; *A.*, ii, 236.

<sup>98</sup> *Zeitsch. Nahr. Genussm.*, 1908, **15**, 75; *A.*, ii, 238.

<sup>99</sup> *Analyst*, 1908, **33**, 184.

<sup>1</sup> *Ibid.*, 313; *A.*, ii, 885

<sup>2</sup> *Chem. Rev. Fett Harz. Ind.*, 1908, **15**, 224.

<sup>3</sup> *J. Russ. Phys. Chem. Soc.*, 1908, **40**, 700; *A.*, ii, 637.

<sup>4</sup> In connexion with the chemistry of Wys' solution, see H. Ingle, *J. Soc. Chem. Ind.*, 1908, **27**, 314.

<sup>5</sup> *Ber.*, 1908, **41**, 19; *A.*, i, 199.

cocoa butter, failed to isolate any constituent to which the characteristic odour could be attributed. From the unsaponifiable matter they isolated amyrlene,  $C_{30}H_{48}$ . H. Matthes and E. Ackermann<sup>6</sup> point out that cocoa fat contains two phytosterols, the acetyl-tetrabromides of which melt at  $180^{\circ}$  and  $132^{\circ}$  respectively. The cholesterol of butter does not form an acetyl-tetrabromide. The ethyl ester value of fats is a new constant devised by J. Hanůs and L. Štekl<sup>7</sup> for the detection of cocoanut oil. C. Fleig<sup>8</sup> has carried out a series of experiments which, on the whole, support Mylius's contention that the Camoin-Baudouin colour reaction of sesamé oil and Pettienkofer's similar reaction of bile acids are due to the furfuraldehyde produced by the mineral acid on the sugar, but the evidence is not conclusive, since lævulose and sucrose give better results than certain pentoses. He also shows that the furfuraldehyde in Villavecchia and Fabris's reagent may be replaced by other aromatic aldehydes.

C. H. Herty<sup>9</sup> draws attention to the wide variations in the optical activity of samples of turpentine from trees grown on the same farm in Florida. F. W. Richardson and J. L. Bowen<sup>10</sup> have investigated various methods of detecting and estimating adulterants in turpentine, one of the conclusions being that refractometric determinations of the distilled fractions give some of the most useful data.<sup>11</sup> C. T. Bennett<sup>12</sup> shows that for the estimation of cineol in eucalyptus oil, Schimmel and Co.'s resorcinol method is untrustworthy, and he points out that the fraction of the oil boiling between  $175^{\circ}$  and  $185^{\circ}$  consists mainly of cineol. A. Bloch<sup>13</sup> estimates citral in lemon-grass oil by removing it as the bisulphite compound. E. M. Chace<sup>14</sup> shows that 2 per cent. of turpentine may be detected in lemon oil by conversion into pinene nitroschloride and examination of the crystals mounted in olive oil under the microscope. P. Jeancard and C. Satie<sup>15</sup> give the optical activity, specific gravity, and ester value of samples of Alpine lavender oil distilled in different years, whilst M. Daufresne<sup>16</sup> has determined some constants of French and German oil of tarragon.

<sup>6</sup> *Ber.*, 1908, **41**, 2000; *A.*, i, 637.

<sup>7</sup> *Zeitsch. Nahr. Genussm.*, 1908, **15**, 577; *A.*, ii, 641.

<sup>8</sup> *Bull. Soc. chim.*, 1908, [iv], **3**, 984, 992; *A.*, ii, 994.

<sup>9</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 863; *A.*, i, 434.

<sup>10</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 613.

<sup>11</sup> See also A. K. Turner, *Oil and Colour Trades J.*, 1908, 503.

<sup>12</sup> *Chemist and Druggist*, 1908, **72**, 55.

<sup>13</sup> *Bull. Sci. Pharmacol.*, 1908, **15**, 72; *A.*, ii, 782.

<sup>14</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 1475; *A.*, ii, 908.

<sup>15</sup> *Bull. Soc. chim.*, 1908, [iv], **3**, 155; *A.*, ii, 232.

<sup>16</sup> *Ibid.*, 300; compare *A.*, i, 436.

S. S. Pickles<sup>17</sup> gives some constants of origanum oil, from which he has isolated a new terpene, origanene.

Among papers dealing with the chemistry of the proteins, the following may be mentioned: G. T. Matthaopoulos<sup>18</sup> makes use of the fact that casein forms a definite compound with sodium hydroxide, in order to estimate it (volumetrically) in milk. His results confirm Laqueur and Sackur's observation that the molecular weight of casein is 1135. C. F. Cross, E. J. Bevan, and J. F. Briggs<sup>19</sup> have extended the work of F. Raschig,<sup>20</sup> and have shown that, like ammonia, the proteins and their derivatives form chloroamines by the action of hypochlorites. These chloroamines liberate iodine from potassium iodide, and the presence of proteins in an organic tissue may be located by first steeping it in an acid solution of bleaching powder, and, after washing, removing the excess of chlorine by immersion in 2 per cent. sodium phosphate solution at 45°, and finally treating it with a solution of potassium iodide and starch: a blue stain will be produced in those parts in which proteins occur. R. H. Aders Pimmer and F. H. Scott<sup>21</sup> find that when phosphoproteins are digested with a one per cent. solution of sodium hydroxide for twenty-four hours at 37°, the whole of the phosphorus is eliminated as phosphoric acid. This serves, therefore, as a means of distinguishing these compounds from the nucleoproteins. S. P. L. Sørensen<sup>22</sup> proposes to measure the amino-acid formed by the hydrolysis of proteins by a method based on H. Schiff's observation that the basic function of these compounds is annulled by the formation of the group  $N:CH_2$  after treatment with formaldehyde, the carboxyl group being then titrated with alkali hydroxide, using phenolphthalein or thymolphthalein as indicator. The reaction of the amino-acids, formaldehyde, and alkali is reversible, but when thymolphthalein is employed as indicator an end point (bright blue colour, obtained by four drops of  $N/5$  barium hydroxide in excess of that required to produce the first colour indication) may be chosen such that the concentration of the hydrogen ions is as low as  $10^{-9.7}$ .<sup>23</sup> To measure the rate of proteolysis, Grützner has proposed to estimate the carmin liberated from fibrin stained with that dye, but H. E. Roaf<sup>24</sup> states that Congo-red may with advantage be substituted for carmin.

<sup>17</sup> *Proc.*, 1908, **24**, 95.

<sup>18</sup> *Zeitsch. anal. Chem.*, 1908, **47**, 492; *A.*, ii, 783.

<sup>19</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 260; *A.*, i, 374.

<sup>20</sup> *Ber.*, 1907, **40**, 4586; *Chem. Zeit.*, 1907, **31**, 126; *Zeitsch. angew. Chem.*, 1907, **20**, 2065; *A.*, ii, 30.

<sup>21</sup> *Trans.*, 1908, **93**, 1699.

<sup>22</sup> *Biochem. Zeitsch.*, 1907, **7**, 45; *A.*, i, 115.

<sup>23</sup> See, further, S. P. L. Sørensen and H. Jessen-Hansen, *ibid.*, 1908, **7**, 407; *A.*, ii, 234.

<sup>24</sup> *Biochem. J.*, 1908, **3**, 188; *A.*, ii, 743.

In the analysis of organic substances, increasing use is being made of physical methods, and numerous papers have appeared recently on the estimation of total solids in molasses, wort, beer, wine, spirits, etc., by means of the refractometer, which can also be used for the estimation of alcohol. The method is principally to be recommended on the score of its rapidity, although in the hands of a skilful worker in a properly equipped laboratory the determination of specific gravity can be carried out very rapidly. On account of the heterogeneous composition of many commercial products, notably the varying amounts of mineral matters present, special tables must be constructed for each kind of product. For practical purposes the assumption that all sugars in solution of like concentration have the same refractive index is quite justified. Tables have been prepared for sugar products by H. Main<sup>25</sup> and by H. C. Prinsen Geerligs.<sup>26</sup> H. Bryan,<sup>27</sup> using Geerligs's tables for honey, syrups, and molasses, finds that the results are in closer accord with the actual determinations of solid matter than are the values obtained by the specific gravity method from Brix's tables. It should be pointed out, however, that this is not due to any defect in the specific gravity method. C. Mai and S. Rothenfusser<sup>28</sup> give a valuable résumé of the application of the refractometric method of detecting the addition of water to milk. From the examination of 5000 samples, they find that the normal refractometer value for milk is 39 divs.; any sample giving a lower reading than 36.5 divs. contains added water. The process fails with sour milks. The application of the method to the estimation of extract in wort is dealt with by O. Mohr,<sup>29</sup> and to that of alcohol and extract in beer and spirits by J. Race.<sup>30</sup> A. Frank<sup>31</sup> observes that the indirect estimation of alcohol by refraction before and after expelling the alcohol is untrustworthy. M. Duboux and P. Dutoit<sup>32</sup> describe a new method of estimating alcohol in wine; it depends on the determination of the temperature at which a clear solution is formed when a fixed amount of the wine distillate is added to a fixed amount of a mixture of aniline or nitrobenzene and alcohol. Some useful data in the pycnometric estimation of alcohol in fermented liquids, with a description of new apparatus, is given by W. Antoni.<sup>33</sup>

<sup>25</sup> *International Sugar J.*, 1907, 9, 481.

<sup>26</sup> *Ibid.*, 1908, 10, 68.

<sup>27</sup> *J. Amer. Chem. Soc.*, 1908, 30, 1443.

<sup>28</sup> *Zeitsch. Nahr. Genussm.*, 1908, 16, 7.

<sup>29</sup> *Wochenach. Brau.*, 1908, 25, 454.

<sup>30</sup> *J. Soc. Chem. Ind.*, 1908, 27, 544, 547; *A.*, ii, 738.

<sup>31</sup> *Chem. Zeit.*, 1908, 32, 569; *A.*, ii, 637.

<sup>32</sup> *Ann. Chim. anal.*, 1908, 13, 4; *A.*, ii, 136.

<sup>33</sup> *J. Amer. Chem. Soc.*, 1908, 30, 1276; *A.*, ii, 902.

M. E. Pozzi-Escot<sup>34</sup> describes a volumetric method of estimating tartaric acid in wine, whilst the Goldenberg method has been investigated by the Chaussele Fabrik vorm. Goldberger, Geromont and Co.,<sup>35</sup> and conditions laid down whereby accurate results may be obtained. L. Gowing-Scopes<sup>36</sup> has submitted J. von Ferentzy's method of estimating tartaric acid in presence of other acids<sup>37</sup> to a critical examination, and finds it trustworthy. A. Hubert<sup>38</sup> has made the interesting observation that citric acid occurs naturally in wines. This has been confirmed by H. Astruc<sup>39</sup> and by G. Denigès,<sup>40</sup> who suggests that the reason the acid cannot be detected in old wines is to be ascribed to bacterial influences. E. Dupont<sup>41</sup> states that Denigès's mercury method of detecting citric acid may be made approximately quantitative. G. Farrel<sup>42</sup> proposes a test which depends on the formation of acetonedicarboxylic acid (when citric acid is heated with sulphuric acid). This ketonic acid gives a violet coloration with ferric chloride.

P. Dutoit and M. Duboux<sup>43</sup> show that by adding successive quantities of barium hydroxide to a wine, and determining its electrical conductivity after each addition, it is possible to estimate consecutively the sulphates, total acidity, and tannin substances present. Under the name of "abristol," calcium  $\beta$ -naphthol- $\alpha$ -sulphonate is added to wine as an antiseptic and precipitant of tartrates. The acid may be extracted by amyl alcohol, and identified by the reddish-violet coloration formed on evaporating with mercurous nitrate.

In connexion with brewing materials, A. C. Chapman<sup>44</sup> has devised a valuable method of estimating tannin in hops by weighing the cinchonine compound, and G. C. Jones<sup>45</sup> has communicated two papers on malt analysis.

The paper by J. S. Ford and J. M. Guthrie,<sup>46</sup> on the biochemistry of barley, adds considerably to our knowledge of the nature of the amylolytic enzyme of barley, and the methods they adopt are most interesting and suggestive. J. Wohlgemuth's suggestion,<sup>47</sup> to measure diastatic activity by estimating the quantity of a diastatic

<sup>34</sup> *Bull. Soc. chim. Belg.*, 1908, 22, 218; *A.*, ii, 740.

<sup>35</sup> *Zeitsch. anal. Chem.*, 1908, 47, 57; *A.*, ii, 237.

<sup>36</sup> *Analyst*, 1908, 33, 315; *A.*, ii, 905.

<sup>37</sup> See *Ann. Report*, 1907, 217.

<sup>38</sup> *Ann. Chim. anal.*, 1908, 13, 139; *A.*, ii, 544.

<sup>39</sup> *Ibid.*, 224; *A.*, ii, 640. <sup>40</sup> *Ibid.*, 226; *A.*, ii, 640.

<sup>41</sup> *Ibid.*, 338; *A.*, ii, 904. <sup>42</sup> *Ibid.*, 177; *A.*, ii, 640.

<sup>43</sup> *Compt. rend.*, 1908, 147, 134; *A.*, ii, 781.

<sup>44</sup> *J. Inst. Brewing*, 1907, 13, 646.

<sup>45</sup> *Ibid.*, 1908, 14, 9, 13.

<sup>46</sup> *Ibid.*, 61; *A.*, ii, 218.

<sup>47</sup> *Biochem. Zeitsch.*, 1908, 9, 1; *A.*, ii, 444.

solution necessary to hydrolyse soluble starch to the stage at which the products no longer give a coloration with iodine, assumes that this is a linear function of the time, which has not been proved, and the same argument applies to W. A. Johnson's method,<sup>48</sup> although this author does compare the iodine results with those obtained by the cupric reduction method. C. J. Lintner<sup>49</sup> shows that the law of proportionality for malt diastase holds good up to a reducing power of 35 (calculated as maltose). He adopts the writer's method of estimating diastatic activity. J. L. Baker and H. F. E. Hulton<sup>50</sup> and J. S. Ford and J. M. Guthrie<sup>51</sup> have published two most important papers on the question of the so-called "strength" of flour in its relation to enzymes. L. Brieger and J. Trebing<sup>52</sup> call attention to the antitriptic power of human blood-serum, and von Bergmann and K. Meyer<sup>53</sup> give a method for the measurement of its activity.

W. Thorner<sup>54</sup> describes a method of estimating water in foods, consisting in distillation with petroleum and collection of the distillate in a graduated receiver, in which the water separates and its volume may be read off. The method is similar to that of Hoffmann,<sup>55</sup> and of Aschman and Arend.<sup>56</sup>

H. D. Richmond,<sup>57</sup> in his annual report on milk, based this year on the analysis of 35,331 samples, adds to our knowledge of the subject. He has examined eight samples of human milk, and points out that the fat varied from 1.7 to 5.7 per cent. He draws attention to a preservative which he has found in certain samples of milk, namely, formic acid, mixed with dextrose. W. R. G. Atkins<sup>58</sup> states that determinations of the freezing point and specific gravity of milk are sufficient to show if water has been added or fat removed. The freezing point of milk is practically a constant, namely, 0.55°.

A. Kreutz<sup>59</sup> shows that after heating cocoa in a flask on the water-bath with chloral alcoholate until a homogeneous paste is obtained, the fat may be extracted by warming with successive quantities of ether. The chloral is all driven off by heating the

<sup>48</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 798; *A.*, ii, 743.

<sup>49</sup> *Zeitsch. ges. Brauwesen*, 1908, **31**, 421.

<sup>50</sup> *J. Soc. Chem. Ind.*, 1908, **27**, 368.

<sup>51</sup> *Ibid.*, 389.

<sup>52</sup> *Berlin Klin. Wochenschr.*, 1908, **45**, 1041.

<sup>53</sup> *Ibid.*, 1673.

<sup>54</sup> *Zeitsch. angew. Chem.*, 1908, **21**, 148; *A.*, ii, 222.

<sup>55</sup> *Wochenschr. Brau.*, 1902, **19**, 372.

<sup>56</sup> *Chem. Zeit.*, 1906, **30**, 953; *A.*, 1906, ii, 814.

<sup>57</sup> *Analyst*, 1908, **33**, 113.

<sup>58</sup> *Chem. News*, 1908, **97**, 241; *A.*, ii, 641.

<sup>59</sup> *Zeitsch. Nahr. Genussm.*, 1908, **15**, 680; *A.*, ii, 641.

fat at 110°. The results agree well with those obtained by the ordinary method. Later,<sup>60</sup> he shows that the theobromine is extracted along with the fat by this method; when treated with carbon tetrachloride the fat alone is dissolved, leaving the theobromine, which may be weighed.

P. Biginelli<sup>61</sup> draws attention to the fact that when tannic acid is used as a precipitant for alkaloids in toxicological investigations, it also forms insoluble compounds with certain solvents and mineral acids. L. Dreyer<sup>62</sup> describes the differentiation of tubercular from ordinary pus by its behaviour towards Millon's reagent. It is well known that the formation of indole from proteins is a characteristic of certain microbes, and C. Porcher<sup>63</sup> proposes to detect indole in pus by its colour reaction with *p*-dimethylaminobenzaldehyde.

ARTHUR R. LING.

<sup>60</sup> *Zeitsch. Nahr. Genussm.*, 1908, **16**, 579.

<sup>61</sup> *Gazzetta*, 1907 **37**, II, 506; *Ch.*, **1**, 40.

<sup>62</sup> *Munch. Med. Wochenschr.*, 1908, **55**, 728.

<sup>63</sup> *Compt. rend.*, 1908, **147**, 211; *Ch.*, **II**, 760.



## PHYSIOLOGICAL CHEMISTRY.

THE output of biochemical papers shows no sign of abatement, and one has also to chronicle the appearance of several new text-books on the subject during the past year. Carl Oppenheimer, of Berlin, is editing a very complete *Handbuch der Biochemie*, which is to consist of twenty parts, and of these six have already appeared. The various articles in it are written by those who have paid particular attention to the portions of the subject on which they write, and the chapters deal with the questions involved from both the chemical and biological point of view. Another new text-book is from the pen of Professor Röhmann. Abderhalden's book has been translated into English, and a second edition of the German version is just to hand. Messrs. Longmans have commenced the issue of a series of important biochemical monographs under the editorship of Drs. F. G. Hopkins and R. H. Aders Plimmer; the first of these is written by Dr. Bayliss, and treats of the enzymes, particularly emphasising the catalytic nature of their action. The next two monographs are by Dr. Plimmer, who deals with the proteins, first as a whole, then of their cleavage products, and finally of the attempts which have been to synthesise them. Dr. H. M. Vernon, of Oxford, has published the lectures he gave at the University of London in the form of a book, entitled "Intracellular Enzymes"; here the part played by ferments in the inner life and metabolism of the cell is described, so far as we can at present recognise such action. Dr. Vernon himself, by his discovery, among other things, of tissue-erepsin, has done much to elucidate this obscure and comparatively new aspect of ferment activity, and of the importance of such action there can be no question. There is, however, a tendency just now to attribute all the chemical transformations which occur during life to enzymatic action, and there is a danger that this idea may be overdone. Ferments may be the exclusive agents which protoplasm employs, but the proof that such agents are really ferments is, in many cases, very insufficient, and it is quite possible that, as knowledge advances, other mechanisms may be brought to light. In the

eighteenth century "vital force" was supposed to be at the bottom of all that could not be otherwise explained, and the conception of a force which no one hoped ever to understand delayed the progress of science. We must take care in the twentieth century that the adoption of a new phrase, "ferment action," is not considered in itself to be a final solution of vital problems. To label any particular chemical change as due to enzymatic activity should be rather a signal for the commencement of renewed research in attempts to understand it still further.

The journal familiarly known as *Hofmeister's Beiträge* has disappeared in the struggle for existence, having been absorbed in the comparatively youthful *Biochemische Zeitschrift*. During the few years this last-named publication has existed, fourteen volumes have already appeared, and if we judge fruitfulness by quantity alone, certainly the *Biochemische Zeitschrift* has been successful in a phenomenal way. If we examine the articles published there, the quality is also of a high standard.

In selecting from the papers of the past year subjects for more detailed and critical review, the difficulty, as usual, arises from an *embarras des richesses*, for hardly any aspect of biochemical knowledge has been omitted from the mass of material published. Most of this relates to subjects which have been previously noticed in these Reports, and works out further details which support or correct views already expressed. This patient exploration of portions of the field which had escaped, or almost escaped, notice before, is most necessary and most praiseworthy, but it must be confessed that, as a rule, it is also extremely dull, and hardly lends itself for interesting treatment in an article of this nature. The activity of many workers among the ferments has already been alluded to. In the forthcoming index Abderhalden's name will loom largely, and his work on the polypeptides and cleavage products of the proteins progresses in a steady stream of published papers; each one of these is a brick in the edifice of knowledge which is slowly being reared, but it may be many years before we are able to obtain a clear view of the final construction. In America, Osborne and his colleagues are pursuing similar work, especially on the vegetable proteins, and data there are being accumulated, the final evaluation of which is also for the future. Nucleic acid, that important appendage of many proteins, has received its due share of attention, and here it does seem that we are in a position at last to reduce the chaos of former years to something like order; nucleic acid, therefore, will form the subject of a fuller paragraph later in this Report. The work of London and his collaborators in their important study of digestion, which formed the subject of a

lengthy section in last year's Report, progresses rapidly, and this list of papers promises to rival in number those of Abderhalden; here again, however, the work has been the pigeon-holing of fresh data, and presents nothing of really new importance; this passing reference will, therefore, be all that I shall attempt this year in relation to this branch of research.

Although so little is known of creatine and creatinine as test-tube products of protein fission, their importance as products of the body's katabolism is rising into prominence. The work directed from so many quarters to the study of these two substances dates a few years back to Folin's investigations, and to the simple methods he then introduced for detecting and estimating them. Although I devoted some pages last year to this subject, it will be necessary to return to it again, because an entirely new light has been shed upon it by the remarkable work which Mellanby is responsible for.

Perhaps, however, the most noteworthy feature of biochemical research to-day is the recognition of the importance of the lipoids in cell life, and, therefore, a section of my Report will be occupied with these materials.

Fresh information on the functions of the pituitary body, hitherto a subject on which we have been almost completely ignorant, has shown us the importance of this gland, both in health and disease. Although the chemical side of the subject is as yet far from clear, I propose to conclude my Report with a brief summary of our present knowledge on this outgrowth of the brain. Without, however, enumerating all the sub-headings of my Report, let us at once proceed to break it up into its various sections, and I will commence with a brief consideration of one I have not yet mentioned, namely:

### *Protein Nomenclature.*

Fellows of the Chemical Society will be well acquainted with the difficulties which attend any efforts at uniformity of terminology, and, although in our own Journal the rules about the use of such terminations as *in* and *ine*, or of *ol* and *ole*, are enforced, the recommendations of the Nomenclature Committee are more often honoured in the breach than in the observance in other publications. This difficulty is enhanced when people speaking and writing other languages are concerned. Although the nomenclature of the proteins is, and probably for long will remain, very unsettled until their constitution is better known, a joint committee of the Chemical and Physiological Societies sat, a year or two ago, to attempt a settlement of the more salient points, and the report

which this committee presented was sent over to America in order to try and obtain uniformity in the use of names between the two great sections of English-speaking men of science. The report was also considered at the International Congress of Physiology, which was held last year at Heidelberg, and although it was not received with enthusiasm, we may, at any rate, claim that the adoption of the word Protein as the title for the great group of albuminous substances by German writers is, at any rate in part, due to our efforts.

But to return to America, for there at least we should hope to be successful, the report was considered by a joint committee of the American Physiological Society and the American Society of Biological Chemists, and during the last year they have published their views.<sup>1</sup> One notes with satisfaction that the American report is in substantial agreement with our own. The points of difference are small ones, and the chief improvement in the American classification is the inclusion of the chief classes of the vegetable proteins; here the hand of T. B. Osborne, who was a member of the American committee, is traceable.

The main points of difference and agreement may be best stated by the following quotations from a report prepared by the Protein Nomenclature Committee of the Physiological Society, which was adopted at a meeting of that Society in May last<sup>2</sup>:

"The term *Albuminoid* is retained for the sub-class named *Sclero-proteins* in the English report. We think the adoption of the new word is preferable to the retention of the old one, because the name albuminoid is still largely used by English and French chemists as synonymous with Protein.

"The only noteworthy difference in the arrangement of the sub-classes is the transference of the phospho-proteins (vitellin-caseinogen group) from the simple to the conjugated proteins. We adhere to the opinion that our own arrangement is better, because the phosphorus-containing group of the phospho-proteins is not split off from them as a true prosthetic group is, and the cleavage products of this class of protein still contain phosphorus.<sup>3</sup>

"A minor difference is the substitution of the term hæmoglobins

<sup>1</sup> *Amer. J. Physiol.*, 1908, **21**, xxvii—xxx; *J. Biol. Chem.*, 1908, **4**, xlviii—li; *A.*, **i**, 301.

<sup>2</sup> *Proc. physiol. Soc.*, 1908, xxxii—xxxv; *J. Physiol.*, **37**.

<sup>3</sup> This view, that phosphorus is part of the protein molecule, and not part of a group such as nucleic acid linked to the protein, is emphasised in Dr. Plimmer's book already mentioned. See also paper by Plimmer (*Trans.*, 1908, **93**, 1500), which treats of vitellin, and also of a second protein in egg-yolk (livetin) which is almost free from phosphorus. See also Plimmer and Scott on the distinctions between phospho-proteins and nucleo-proteins (*ibid.*, p. 1699).

for the class called chromo-proteins in the English report. We prefer the latter name as having the wider significance.

"Five additional substances are introduced at various places in the American report. These are:

"1. The *glutelins*, the alkali-soluble proteins of vegetable origin.

"2. The *alcohol-soluble proteins* found in the vegetable world.

"We think the inclusion of these two new classes of simple proteins (and especially the latter) is advantageous, as it makes the system more complete. We are prepared to accept, provisionally, the term glutelin for the proteins soluble in alkali, although they are doubtless closely allied to the globulins. The term alcohol-soluble proteins strikes us as rather cumbrous; these substances might, as Rosenheim<sup>4</sup> has suggested, be termed *gliadins*; that is, the name of the principal member of the group might be extended to serve as a class name.

"3. The *lecitho-proteins* are added to the classes of conjugated proteins. As it has not yet been decided whether these are mechanical mixtures, adsorption compounds, or true chemical combinations, we see no reason for the inclusion of this group.

"4. The *proteans*: insoluble products which 'apparently result from the incipient action of water, very dilute acids or enzymes.'

"5. *Coagulated proteins*: which result from the action of heat or of alcohol.

"Sub-classes 4 and 5 are placed among the primary protein derivatives; they are of an ill-defined nature, and we see no object in singling out for special mention a few of the infinite varieties of insoluble modifications which proteins exhibit."

The final result of this consultation with our American *confrères* is the classification of proteins into the following groups:

1. Protamines.
2. Histones.
3. Albumins.
4. Globulins.
5. Glutelins.
6. Gliadins.
7. Phospho-proteins.
8. Sclero-proteins.
9. Conjugated proteins:
  - a. Nucleo-proteins.
  - b. Chromo-proteins.
  - c. Gluco-proteins.

<sup>4</sup> *Proc. physiol. Soc.*, 1908; *J. Physiol.*, **36**, 1v; *Science Progress*, 1908, **2**, 696.

## 10. Protein derivatives:

- a. Meta-proteins (acid-albumin, etc.).
- b. Proteoses.
- c. Peptones.
- d. Polypeptides.

It is, of course, impossible, at this stage in the history of protein-chemistry, to obtain absolute unanimity on minor points of classification and nomenclature; but the system is now complete for practical purposes, and its utility can only be proved by giving it a fair trial. In the new text-books on the subject, it is already being adopted.

*Caseinogen and Rennin.*

It is an undoubted fact that the milk provided by Nature for the growing offspring is different in the various classes of the animal kingdom. The quantitative variations are often enormous, and it has been shown that the milk best adapted for the nutrition of the young animal is that which comes from its mother, or, at least, from an animal of the same species. The practical application of this rule comes home to most of us when dealing with the feeding of children, and it is universally acknowledged that, after all, cows' milk is but a poor substitute for human milk. Cows' milk is, of course, diluted, and sugar and cream added, so as to make it quantitatively like mothers' milk, but even then the question arises whether the essential difference between the two kinds of milk is not deeper than one of mere quantity; and, in particular, the pendulum of scientific opinion has swung backwards and forwards in relation to the question whether the principal protein, called caseinogen, in both is really identical in the two cases. The caseinogen of human milk curdles in small flocculi in the stomach, so contrasting with the heavy curd which cows' milk forms; and even although the curdling of cows' milk be made to occur in smaller fragments by mixing the milk with barley-water or lime-water, its digestion proceeds with comparative slowness in the child's alimentary canal. These are practical points well known to every clinical observer, and in the past they have been attributed, not so much to fundamental differences in the caseinogen itself, as to accidental concomitant factors; the excess of citric acid in human milk, for instance, or its paucity in calcium salts, having been held responsible for the differences observed in the physical condition of the curd and in its digestibility.

This question is far from settled even to-day, but there are

some data now available that point to a qualitative difference between caseinogens. Some of these depend on the application of the "biological test" carried out on the line of immunity experiments, which method has been so signally successful in the distinction between the blood-proteins of different species of animals. The differences, however, which lead to the formation of specific precipitins are so slight, that ordinary chemical methods of analysis are, at present, unable to reveal them. But, in the case of milk, there are differences which the chemist can detect. One cannot lay much stress on mere percentage composition, although differences have been noted in that, because we have no guarantee that the proteins investigated were separated from all impurities. Differences are also noticeable in the yield of monoamino-acids, but the methods at present employed in the estimation of these cleavage products are far from perfect. A deeper chemical distinction noted is, however, mentioned in the recent work of Bienenfeld,<sup>5</sup> who find that human caseinogen contains a carbohydrate complex, which, as is well known, is absent from that of the cow.

A few years ago it was stated that human caseinogen will not curdle with rennet, and Bienenfeld upholds this view; but it appears to be a mistake. The conditions of rennet curdling are somewhat different in the two kinds of milk we are considering, and the factors concerned in this phenomenon in human milk have been worked out by Jacoby,<sup>6</sup> who has paid special attention to the action of anti-rennin, by Fuld and Wohlgemuth,<sup>7</sup> who criticise Bienenfeld's observations, and by Engel,<sup>8</sup> who deals mainly with the influence of reaction.

Another problem closely related to the preceding is the view we are to take of the ferment rennet or rennin itself. Hammarsten's authority is the one usually relied on for the statement that gastric juice contains two distinct enzymes, pepsin, the proteoclastic ferment, and rennin, the milk-curdling one. It was Pawloff who first suggested that the rennetic action was the work also of the peptic enzyme; and Ehrlich's convenient side-chain theory was considered to explain the double action, the curdling being the result of the activity of one or more molecular groups in the pepsin molecule. It is a little early to argue in this manner, for, as Emil Fischer so wisely said in his Faraday lecture, nobody has yet ever been successful in separating out any enzyme in a state of purity. For the same reason, one must feel chary in accepting as proved the recent statements made by

<sup>5</sup> *Biochem. Zeitsch.*, 1907, 7, 262; *A.*, ii, 121.

<sup>6</sup> *Ibid.*, 1908, 8, 40; *A.*, i, 236.

<sup>7</sup> *Ibid.*, 376; *A.*, ii, 311.

<sup>8</sup> *Ibid.*, 1908, 13, 89; *A.*, ii, 878.

Scala,<sup>9</sup> that rennin is a weak base consisting of a proteose nucleus and amino side-chains. However this may be, Gewin<sup>10</sup> has championed Pawloff's view, and maintains that pepsin and rennin are one and the same ferment. He regards the rennet action as the first stage in the digestion of caseinogen. If hydrogen ions are absent and calcium ions are present, digestion stops and a curd separates, but if a sufficient number of hydrogen ions are present, ordinary peptic digestion proceeds.

Unfortunately, there appear to be as many and as eminent authorities ranged on the opposite side, and during the last year I. Bang<sup>11</sup> and Hammarsten<sup>12</sup> himself have published papers which conclude that the two ferments are not identical.

The question is an interesting one, and, perhaps, in some future year, we shall be able to relate how it has been finally settled.

*Plasteins*.—It has long been known that the addition of rennet to a solution of "peptone" causes the formation of a precipitate, and the name plastein was given to the precipitated substance. The same occurs when gastric juice, or pepsin-hydrochloric acid, is added to "peptone" solution, so the formation of plastein is not distinctive of rennet, even if that enzyme is not identical with pepsin. When the discovery was first made, it was supposed that one of the actions of the rennetic enzyme was to produce the "regeneration of albumin"; this was at a date when the exclusive seat of the synthesis of protein from its cleavage products was supposed to be the wall of the alimentary canal, the seat of absorption. Recent research has done something to confirm this view of the composition of plastein, but in modern terminology we speak of it now as the reversible action of the enzyme concerned. This view is taken by Sawjaloff,<sup>13</sup> and the analytical figures he gives indicate that the reaction is either bimolecular or termolecular. Plastein is, therefore, the result of the union of either two or three molecules of the proteoses from which it is formed, and its molecular weight is, on the average, twice that of the proteoses. The plasteins used were prepared from a large range of proteins, and an attempt is made to classify them. Levene and van Slyke<sup>14</sup> have made similar experiments, and obtained the cleavage products of plastein; these include both mono- and di-amino acids; the total yield, however, only amounted to 39 per cent. Their conclusion as to the composition of plastein is different from that of Sawjaloff; they regard it as a complex protein not far removed in composition from fibrin,

<sup>9</sup> *Staz. sperim. agrar. ital.*, 1907, 40, 129; *A.*, i, 236.

<sup>10</sup> *Zeitsch. physiol. Chem.*, 1907, 54, 32; *A.*, i, 71

<sup>11</sup> *Ibid.*, 359; *A.*, i, 236.

<sup>12</sup> *Ibid.*, 56, 18; *A.*, i, 588.

<sup>13</sup> *Ibid.*, 54, 119; *A.*, i, 234.

<sup>14</sup> *Biochem. Zeitsch.*, 1908, 13, 458; *A.*, i, 932.



but they were unable to decide whether it is a synthetic product, or a coagulated form of one of the fibrin proteoses.

Lawroff<sup>15</sup> appears to have been more successful in formulating general views of the composition of these substances, although it is to be regretted that he has introduced confusion by the coining of a new name for them. He obtained these precipitates (which he calls coaguloses) by the peptic digestion of proteins, as well as by their digestion in dilute mineral acids. He recognises two types of coagulose-yielding substances; the first are of the type of proteoses, and the coaguloses which arise from them yield, on hydrolysis, both monoamino-acids and basic cleavage products. The second type of coagulose-yielding substances are polypeptides, and the coaguloses which arise from them yield, on hydrolysis, only monoamino-acids. The proteins which Lawroff first worked with were caseinogen and hæmoglobin, but subsequent work<sup>16</sup> with crystallised egg-albumin showed that the same two types of coagulose-yielding substances could also be obtained from this protein after relatively short peptic digestion.

These facts and theories are worthy of record, but I do not fancy the last word on plasteins or coaguloses has yet been written.

### *Nucleic Acid.*

Nucleic acid has, in the past, been prepared from many different sources, and differences have been noted in its percentage composition and in its decomposition products. It has, therefore, been assumed that there are many varieties of nucleic acid, all resembling each other in containing phosphorus, in yielding purine and pyrimidine bases, and in containing a carbohydrate radicle, usually described as a pentose. The differences observed have been considered to be mainly due to the proportion in which these various groups are combined together, and more especially to the nature of the purine and other bases contained within the molecule. It need hardly be said that if this view is correct, the complexity of the subject is enormous. But, as the years go by, and better methods for the separation and purification of nucleic acid are introduced, these difficulties are beginning to be cleared up, and nucleic acids previously supposed to be different are now to be regarded as identical. Schmiedeberg<sup>17</sup> has been able to give an empirical formula for the acid; and Levene and Mandel<sup>18</sup> have even advanced views as to its constitution, which

<sup>15</sup> *Zeitsch. physiol. Chem.*, 1907, **53**, 1; *A.*, 1907, i, 995.

<sup>16</sup> *Ibid.*, 1908, **56**, 343; *A.*, i, 844.

<sup>17</sup> *Arch. exp. Path. Pharm.*, 1907, **57**, 309; *A.*, i, 70.

<sup>18</sup> *Ber.*, 1908, **41**, 1905; *A.*, i, 587.

probably should be regarded more safely as provisional than final. Schmiedeberg, also, in his work has drawn attention to what he regards as a distinction between the hydrated and anhydrous forms of the acid, and to the power which the latter possesses of gelatinising. This recognition of a gelatinous condition sometimes presented by nucleic acid and its salts is of importance, whether the explanation that the absence or presence of water in the molecule is the correct one or not.

A greater advance than this, however, was made a few years back by I. Bang. He prepared, from the nucleo-protein of the pancreas, a nucleic acid which is much simpler in composition than the majority of those previously investigated. It yields on decomposition three substances, namely, phosphoric acid, pentose, and only one purine base, guanine. For this reason, he bestowed upon it the name of guanylic acid. He also mentioned a fourth cleavage product, glycerol, but this has not been obtained by subsequent workers, for instance, by Steudel,<sup>19</sup> who otherwise confirms Bang's results. The question was also taken up by v. Fürth and Jerusalem,<sup>20</sup> who at first denied the existence of guanylic acid altogether. Bang<sup>21</sup> pointed out how they had erred, and on re-investigating the matter they acknowledged their mistake,<sup>22</sup> and confirmed Bang's statement, with the exception, again, that glycerol was not found among the decomposition products of guanylic acid.

Since then, guanylic acid has been found in other organs, for instance, in the liver, by Levene and Mandel.<sup>23</sup>

Both liver and pancreas, however, contain, in addition to guanylic acid, what we may term ordinary nucleic acid, which yields on cleavage other bases.

These observers have, therefore, cleared up one previous source of error; there is no doubt that the older workers investigated mixtures of nucleic acid proper and guanylic acid, and thus obtained divergent analytical results. The discovery of guanylic acid at first seemed to complicate the subject, but, really, it helped to elucidate it.

The next step was taken by Walter Jones,<sup>24</sup> who, following up the work of Schmiedeberg already referred to, has established the

<sup>19</sup> *Zeitsch. physiol. Chem.*, 1907, 53, 539; *A.*, i, 70.

<sup>20</sup> *Beitr. chem. Physiol. Path.*, 1907, 10, 174; *A.*, 1907, i, 993.

<sup>21</sup> *Ibid.*, 1907, 11, 76; *A.*, i, 70.

<sup>22</sup> *Ibid.*, 1908, 11, 146; *A.*, ii, 119.

<sup>23</sup> *Biochem. Zeitsch.*, 1908, 10, 221; *A.*, i, 587. They also describe a new method for the separation of guanine (*ibid.*, 215; *A.*, i, 586). Guanylic acid has also been discovered in the spleen, mammary gland, etc.

<sup>24</sup> *J. Biol. Chem.*, 1908, 5, 1; *A.*, i, 744.

identity of at least three ordinary nucleic acids, namely, those from the thymus, spleen, and pancreas. We need not follow him into the interesting historical review of the curious "comedy of errors" which led to previous confusion. Most of these were due to the different methods employed for isolating these substances, to the difficulties in estimating their cleavage products, to the non-recognition that certain bases are not primary cleavage products but arise by secondary reactions, and last, but not least, to admixture with guanylic acid. The special points worked out in determining the identity of these acids were their specific rotation under varying conditions, and the degree of viscosity of their sodium salts. The so-called gelatinous sodium salt and the non-gelatinous salt are readily convertible one into another, and this reversible action is believed to be a simple explanation, if it occurs *in vivo*, of the physiological localisation and migration of nucleic acid.

He also states the following propositions, derived partly from Schmiedeberg's work and partly from his own, as being, at any rate, not far from correct:

1. All "ordinary nucleic acids" (that is, nucleic as opposed to guanylic acid) yield the same two purine bases (guanine and adenine) and in the same proportion. Xanthine and hypoxanthine, when present, are due to the secondary action of de-amidising ferments.

2. All yield the same pyrimidine base, cytosine.

3. All yield lævulic acid. This was first demonstrated by Kossel, and points to the existence of a "hexose" carbohydrate. The previous statements about the presence of a pentose are, no doubt, due to admixture with guanylic acid.

4. There is, therefore, no insurmountable difficulty in accepting the hypothesis that the nucleic acids of different mammalian organs are identical substances. One must, however, be cautious at present in applying this generalisation to all nucleic acids, for it has been shown that those derived from plants and from fish eggs yield uracil, and that from the spermatozoa of fishes yields thymine, another pyrimidine base. Uracil obtained from mammalian nucleic acid is derived secondarily from cytosine.

5. The furfuraldehyde reaction stated to be given by nucleic acids is probably owing to admixture with guanylic acid, and due to the guanine and pentose present.

#### *Tissue Metabolism.*

Metabolism was at one time only studied by what is called the balance-sheet method. The total ingesta and egesta were measured

and analysed, and by this means it was ascertained whether the body was in equilibrium, or whether a deficit or the reverse was occurring in connexion with the main groups of body-constituents. Valuable as this method was, more important information still is obtainable by the investigation either of individual tissues or organs, or in relation to the utilisation of one or other constituent of the food. It is this modern method of working at the subject which has been successful in determining, not only the special functions of each organ under varying conditions, but also the rôle played by the individual food-stuffs in their internal chemical changes.

Many gaps exist in our knowledge still, but these are, year by year, becoming less numerous, and from the large mass of work which has accumulated during the last twelve months, I am only able to select a few papers which appear to be of exceptional interest.

*Respiration.*—The work of Haldane and Priestley<sup>25</sup> on the importance of the chemical factor in breathing has been a great stimulus to renewed work on the subject of respiration generally. Those who attend the meetings of the Physiological Society will know the frequent discussions that occur there on the points which still remain in dispute. I think, however, that Haldane's contention, that variations in the tension of carbon dioxide in the pulmonary alveoli form the essential factor, has been very generally conceded. The differences in the alveolar tension of this gas affect the respiratory centre *viâ* the blood-stream, and carbon dioxide is the chemical stimulus *par excellence* which regulates the work of the respiratory centre in the brain. The points on which difference of opinion still prevails are: (1) the part played by a diminution of oxygen; (2) the relative importance of the nervous factor; and (3) whether fatigue products, such as lactic acid, may assist the carbon dioxide in stimulating the respiratory centre.

One notes an interesting piece of work relating in the main to the second of these disputed problems by F. H. Scott.<sup>26</sup> From this work it appears that the principal respiratory nerves (the pneumo-gastrics) regulate the rate or rhythm of the respiratory movements, whilst the chemical factor specially regulates the amount of pulmonary ventilation, that is, the depth of the individual respiratory efforts; for when these nerves are divided, a rise in the alveolar tension of carbon dioxide (or *great* diminution of

<sup>25</sup> See *Ann. Report*, 1905, 230.

<sup>26</sup> *J. Physiol.*, 1908, **37**, 301; *A.*, ii, 865. A series of papers by Haldane and others on the question of pulmonary ventilation has also just been published (*J. Physiol.*, 1908, **37**, 355; *A.*, 1909, ii, 66) too late for fuller notice here.

the oxygen in the respired air) increases the depth, but not the rate of breathing. The vagi in reference to respiration are regarded in the same light as the sensory nerves of muscle; without these nerves, muscular movements are excessive and even ataxic.

Such researches have also cleared up the mechanism of Cheyne-Stokes breathing, that curious waxing and waning of the respiration which is seen slightly during normal sleep, and markedly in the hibernating state of winter-sleeping animals, as well as in many pathological states in man (Pembrey<sup>27</sup>).

The condition common to all these states is a decreased excitability of the nervous system, and especially of the respiratory centre. The man or the animal does not breathe for a certain period, and during this apnœic stage, carbon dioxide accumulates until its amount is sufficient to stimulate the depressed cells of the respiratory centre to execute shallow and inefficient efforts at breathing; but as the accumulation of the gas goes on, the respirations become more and more forcible, and culminate in forced or dypnœic breathing; this sweeps out the carbon dioxide, and the convulsive movements become quieter, the breathing gets shallower, and, finally, it once more ceases for a period, until the same series of events is again repeated.

*The Part Played by Leucocytes in Protein Absorption.*—The entrance of oxygen by the lungs is, of course, only the start of the true respiratory process which occurs in the tissues. The entrance of protein by the alimentary tract is, also, only the initial stage of protein metabolism. In last year's Report I dealt with this question, and so it will not be necessary to repeat myself. Dr. Pavy, in some recent lectures published in the *Lancet*,<sup>28</sup> however, dissents from the view now gaining credence among physiologists, that the proteins are absorbed as amino-acids. He holds the older view, that the intestinal wall is the seat of protein synthesis, and, further, that the lymphocytes play an important part as protein-carriers. This last hypothesis has received support from the work of Cramer and Pringle,<sup>29</sup> who emphasise, as Pavy does, the increase in these cells which occurs whether the protein be introduced in the usual way or parenterally. The blood of digesting animals shows a small but distinct increase of "residual nitrogen" over that of fasting animals, and the major part of this is in the corpuscular elements. It is impossible to deny that the increase in lymphocytes during absorption has some significance, but their total bulk is so small that it is difficult to believe that

<sup>27</sup> *J. Path. Bact.*, 1908, 12, 258; *A.*, ii, 204.

<sup>28</sup> November and December, 1908.

<sup>29</sup> *J. Physiol.*, 1908, 37, 146; *A.*, ii, 709.

they carry the whole burden, and, therefore, Cramer's conclusion that these cells "partly, at any rate," may perform a share of the work, is probably all that it is safe to affirm at present. It will, however, be noticed that such increase in nitrogen as can be determined is in "residual," not in "coagulable nitrogen." Cramer, therefore, does not go as far as Pavy, for protein synthesis, according to him, does not occur at the seat of absorption, or even after ingestion by the colourless corpuscles.

*Respiratory Metabolism of the Spinal Cord.*—The gaseous metabolism of nervous tissues is, perhaps, the most difficult of all subjects to investigate, but by the use of Thunberg's micro-respirometer,<sup>30</sup> it has been shown that even peripheral nerves participate, to some extent, in respiratory interchanges. We should anticipate, on a priori grounds, that the more vascular central nervous material would be more active in this direction; we, at any rate, know that if the brain is deprived even momentarily of its due supply of fresh oxygen, unconsciousness or fainting is the result. Mosso, also, some years ago stated that the temperature of the brain is a high one, and during the last year Winterstein<sup>31</sup> has subjected the isolated fresh spinal cord of the frog to quantitative experiment; he found that, on stimulation, it has a high respiratory exchange; per unit of weight this is two or three times greater than that of the body as a whole. Curiously enough, stimulation by the administration of strychnine was not found to have any effect.

*Rate of Conduction in Nerve.*—An indirect means of approaching the question whether any given phenomenon is chemical or physical is the method of determining the temperature-coefficient of its velocity. Arrhenius showed that the rapidity of a chemical reaction is at least doubled by a rise of  $10^{\circ}$  in temperature, whereas a physical reaction is not accelerated in nearly so great a proportion. Synder<sup>32</sup> has used this method in relation to a number of physiological phenomena, and although his data are, in many cases, insufficient to draw conclusions from them, he nevertheless showed that, in cases where it is known that metabolism does occur, the coefficients observed are those of chemical reactions.

The method, therefore, appears to be one which possibly may settle the vexed question whether the propagation of the nervous impulse is chemical or physical. Maxwell<sup>33</sup> made experiments on the pedal nerve of a giant slug; he selected this, first, because it

<sup>30</sup> *Ann. Report*, 1905, 231.

<sup>31</sup> *Zentr. Physiol.*, 1908, 21, 369; *A.*, ii, 509.

<sup>32</sup> *Amer. J. Physiol.*, 1908, 22, 309; *A.*, ii, 768.

<sup>33</sup> *J. Biol. Chem.*, 1907, 3, 359; *A.*, 1907, ii, 977.

is a sufficiently long nerve, and secondly, because the normal rate of conduction is sufficiently slow for purposes of measurement. From his figures he concludes that the nerve impulse is a chemical phenomenon, although he doubts whether it is an oxidation process. These experiments have been repeated by Woolley<sup>34</sup> on amphibian nerve, and although he obtains the same figure as Maxwell (1.78 to 1.79), he is, unfortunately, not so clear as to its interpretation, for he doubts whether the high figure is a necessary proof of a chemical as opposed to a physical process. The conduction rate in amphibian muscle has about the same coefficient (1.79 to 2.01). It is pretty certain that muscular conduction has an underlying chemical basis, and probably the conduction process is similar in both tissues. The coefficient for the latent period of muscle is distinctly higher (3.26 to 3.3), and this result strengthens a supposition previously advanced on other grounds that conduction in muscle is a propagation, not of the contractile change, but of an independent disturbance which elicits the contractile change at each point on its passage.

*Glycogen.*—This subject is one of perennial interest in relation to metabolism, and some observations on rabbits made by Lochhead and Cramer<sup>35</sup> furnish a useful contribution to the chemistry of growth. In the foetal condition, the greater part of the placental glycogen was found in the maternal portion of the placenta; this diminished from the eighteenth day of foetal life onwards, whereas that in the foetal liver increased. A distinct parallelism was found between the growth of the foetus and the amount of glycogen which it contains. In the earlier stages of intra-uterine life, the foetal liver does not possess the power of storing glycogen; this power is not acquired until the last week of gestation. During the earlier period, the placenta fulfils the hepatic function so far as glycogen is concerned. Investigations on the effect of diet and phloridzin appear to show that the glycogen metabolism of the placenta and foetus is independent of that of the mother.

Pflüger<sup>36</sup> seems to have published only one paper on glycogen this year; he finds that the administration of lævulose leads to the formation of glycogen in the liver, but the glycogen formed is not lævorotatory; the liver cells have, therefore, the power of transforming the sugar given into dextrose, and it is this from which the glycogen is formed.

His colleague at Bonn, K. Grube,<sup>37</sup> has continued his interesting

<sup>34</sup> *J. Physiol.*, 1908, **37**, 112, 122; *A.*, ii, 711.

<sup>35</sup> *Proc. Roy. Soc.*, 1908, **80**, B, 263; *A.*, ii, 710.

<sup>36</sup> *Pflüger's Archiv*, 1908, **121**, 559; *A.*, ii, 307.

<sup>37</sup> *Ibid.*, 636; *A.*, ii, 307.

experiments on the perfusion of the tortoise's liver, and, in answer to the question what is the smallest molecule from which the liver can make glycogen, finds that by perfusing that organ with a weak formaldehyde (0.01–0.02 per cent.) solution, the liver is able to make glycogen from it.

*The Role of Sugar in Muscular Activity.*—In confirmation of the view, now so generally held, on the importance of sugar as the source of muscular energy, Locke and Rosenheim's<sup>38</sup> results on the isolated mammalian heart must be noted. They describe an ingenious new perfusion method<sup>39</sup> by which a solution of dextrose in oxygenated Ringer's solution can be repeatedly circulated through an excised rabbit's heart. Five to ten centigrams of the sugar disappear in from eight to nine hours. This is not due to minor metabolic or fermentative by-processes, but is associated with the main chemical change that underlies cardiac activity. If the activity of the heart is lessened by the omission of the calcium, or still more by the omission of both calcium and potassium from the circulating fluid, the amount of sugar used up is lessened. The amount of carbon dioxide formed runs parallel with the disappearance of sugar. No evidence was found of the formation of disaccharide or of lactic acid, or of the storage of glycogen in the heart. Nitrogenous waste was not fully investigated, but the total is extremely small.

The last aspect of the subject has been taken up incidentally in a piece of work just published by Howell and Duke.<sup>40</sup> These authors had previously stated that an output of potassium from the heart's substance occurs during vagus inhibition, and suggested that the increase in cardiac activity which follows stimulation of its accelerator nerves may be due to an output of calcium. Using the Locke-Rosenheim method of perfusion just referred to, their findings, however, were negative; neither the calcium nor the potassium in the circulating fluid showed any variation in amount after a perfusion lasting for hours, nor after long-continued excitation of the heart through its accelerator nerves.

In relation to nitrogenous metabolism, they found no output of hypoxanthine, such as Burian has described in the case of skeletal muscle. This may be a fundamental distinction between the two forms of muscular tissue, or it may be due to the presence of dextrose in the circulating fluid used by Howell and Duke, which was absent in Burian's experiments. The heart, however,

<sup>38</sup> *J. Physiol.*, 1907, **36**, 205; *A.*, ii, 120.

<sup>39</sup> Brodie and Miss Cullis have also described a new apparatus for the heart-perfusion (*ibid.*, 1908, **37**, 387; *A.*, ii, 865).

<sup>40</sup> *Amer. J. Physiol.*, 1908, **23**, 174; *A.*, 1909, ii, 72.



gives off creatinine (or creatine) to the circulating fluid, and it will be interesting to determine how far this elimination is associated with functional activity.

*Creatine and Creatinine.*

Creatine is absent from normal urine and creatinine is always present. It is, in fact, next to urea, the most abundant nitrogenous substance found there. Amid all the inconstancies of urinary composition, it appears to be the substance which is most constant in amount, diet and exercise having no effect on it. The old idea that the bulk of the urinary creatinine is derived from the creatine of flesh food has been entirely abandoned, and Folin's view that it is a measure of endogenous nitrogenous katabolism has steadily gained ground. The close chemical relationships of the two substances in question led physiologists to the erroneous conclusion that creatine is the source of the excreted creatinine. The discovery of the mistake has led some to the equally hasty conclusion that the two materials have no physiological connexion at all. A relationship does exist between them *in vivo*, but it is a different one from that previously supposed to exist. During the past year, the papers relating to this subject have been numerous, and although differences of opinion on points of detail are noticable, the general trend of most of the results is the same.

Taking Mellanby<sup>41</sup> first, he took as his starting-point an investigation of the contradictory data relating to the proportion of creatine and creatinine in muscle. Monari's authority is usually quoted for the text-book statement that the latter increases at the expense of the former when muscle becomes active. Mellanby has shown that this is not the case. Monari's technique affords an opportunity for the change to occur, and his precipitates were impure. Creatinine is never present in muscle at all, even after prolonged muscular work; the original amount of creatine remains unaltered by work, and even (in frog's muscle) after survival for three days.<sup>42</sup>

In addition to this, aseptic or antiseptic autolysis causes no change in either creatine or creatinine. When, however, the muscle becomes septic, all the creatine disappears. The statements of Gottlieb and Stangassinger<sup>43</sup> regarding the tissue enzymes they term creatase and creatinase were in no respect confirmed.<sup>44</sup>

<sup>41</sup> *J. Physiol.*, 1908, 36, 447; *A.*, ii, 308.

<sup>42</sup> Cathcart and Graham Brown, however, discovered a slight increase of creatinine in frog's muscles after stimulation; but if the circulation is intact there is a decrease (*Proc. physiol. Soc.*, 1908, xiv—xv; *J. Physiol.*, 37; *A.*, ii, 516).

<sup>43</sup> *Ann. Report*, 1907, 239.

<sup>44</sup> Gottlieb and Stangassinger have published a second paper on these ferments;

Invertebrate muscle contains no creatine, and Mellanby selected the developing bird in which to study the biochemical history of creatine. It is absent from the musculature of the chick up to the twelfth day of incubation; after this date, the liver and the muscular creatine develop *pari passu*. After hatching, the liver still continues to grow rapidly, the creatine percentage in the muscles increases also, although the development of the size of the muscles occurs very slowly. This led Mellanby to the conclusion that the muscular creatine has its origin in the liver. The liver is thus continuously forming creatinine from substances carried to it by the blood from other organs; in the developing muscles this is changed to creatine, and then, when the muscle is saturated with creatine, excess of creatinine is excreted by the kidneys. His view is, therefore, an absolute reversal of those previously held; the muscles do not change creatine into creatinine, but creatinine into creatine. If creatine (an innocuous neutral substance) was converted by the muscles into creatinine (a strongly basic substance), it would really be contrary to all that is known of the chemical changes which occur in the body.

This view is upheld by experiments in which creatine and creatinine were added to the food; feeding with the latter substance leaves the muscles still free from that material. Feeding with creatine has also no effect after the muscles have reached a certain point of saturation.

The small amount of creatinine excreted in diseases of the liver also supports the view that that organ is responsible for creatinine formation. The excretion of creatine in cancer of the liver is explained by supposing that the muscle cells break down, and that creatine is liberated without conversion into creatinine before excretion takes place.

Verploegh and van Hoogenhuyze<sup>45</sup> have published an extensive series of observations on creatinine excretion; they confirm Folin's views in the main, and also agree with Mellanby concerning the importance of the liver in its metabolic cycle. Their reference to Mellanby's views, however, appears to contain a misunderstanding, for they allude to the conversion of creatinine into creatine by the liver, which was not Mellanby's point at all. This change they

they attribute the destruction of creatinine and the consequent appearance of creatine which liver extracts accomplish to the action of creatinase, and the subsequent destruction of creatine to creatase (*Zeitsch. physiol. Chem.*, 1908, 55, 295, 322; *A.*, ii, 515). Their statements regarding the non-participation of putrefaction in this ferment action are confirmed by Rothmann (*ibid.*, 1908, 57, 131; *A.*, ii, 967). That the transformation of creatine into creatinine in the liver is the work of soluble ferments is also confirmed by van Hoogenhuyze and Verploegh (*ibid.*, 161; *A.*, ii, 971).

<sup>45</sup> *Loc. cit.*

attribute to the creatinase of Gottlieb and Stangassinger,<sup>46</sup> and in conditions where hepatic activity is lowered (cancer of the liver, certain fevers, and hunger), the appearance of creatine in the urine<sup>47</sup> is explained by its non-conversion into creatinine.

Mellanby's views will, of course, have to be subjected to the usual tests of criticism and renewed research, and, until they have stood this, cannot be accepted as proved. They nevertheless provide a stimulus to fresh work, and their novelty, and the fact that they do explain some of our previous difficulties, render them attractive.

Shaffer,<sup>47</sup> for instance, has independent opinions. He entirely dissents from Mellanby's theory that creatinine is formed in the liver at all; neither does he agree with Folin that its amount is an index of endogenous protein metabolism. He, however, confirms previous statements regarding the constancy of its amount, and he places the figure at from 7 to 11 milligrams of creatinine nitrogen excreted per diem per kilo. of body-weight. The excretion is constant, not only from day to day, but from hour to hour; it is not influenced by the volume of the urine, nor by the total nitrogen excreted. The creatinine coefficient is parallel to the muscular efficiency of the individual, and its source is some special process of muscular metabolism. But in acute fevers, he states that its excretion is increased, and admits that here it is not parallel to muscular efficiency. Creatine is absent from normal urine, but it may be excreted in acute fevers, in women during involution of the uterus, and in certain other conditions in which there is a rapid loss of muscle-protein.

Shaffer is not the first who has pointed out a parallelism between creatinine excretion and muscular development.<sup>48</sup> The small amount in infants' urine corresponds with the smaller amount of muscular development in the child. The amount of creatinine in infants' urine is so small that some previous observers, using the old zinc chloride method, missed it altogether. Funaro<sup>49</sup> has always found it present, and its amount constant, in spite of variations in the food.

Another lengthy paper on creatinine metabolism has recently appeared by G. Lefmann.<sup>50</sup> The following are its principal conclusions: The excretion of creatine and creatinine is pretty constant in well-nourished animals. If either substance is added to the food, it is excreted unchanged. If creatine is given by the mouth, or parenterally, it is never changed into creatinine, and

<sup>46</sup> See footnote 44.

<sup>47</sup> *Amer. J. Physiol.*, 1908, 23, 1; *A.*, ii, 971.

<sup>48</sup> See Spriggs, also Amberg and Morrill, *Ann. Report*, 1907, 238.

<sup>49</sup> *Biochem. Zeitsch.*, 1908, 10, 467; *A.*, ii, 716.

<sup>50</sup> *Zeitsch. physiol. Chem.*, 1908, 57, 476; *A.*, ii, 1050.

in inanition it is almost completely excreted as such. Disease of the liver or increased protein katabolism produces, first an increase, then a decrease in creatinine excretion, and when it is lessened, the amount of creatine excreted rises. The liver is the probable seat of creatinine formation. If nephritis is induced by chromates, nearly all the creatinine is changed into creatine, probably by the alteration in the reaction of the urine.

I have been content merely to enumerate Lefmann's conclusions without comment; some agree with, some differ from, those enunciated by others, and the last one opens up a new possibility. None of the papers written (except that of Mellanby) has presented a clear and consecutive view of the history of creatinine, and although some of his views may have to be modified in the future, there is a general consensus of opinion now that the liver plays an important share on the constructive side of its metabolism.

#### *The Lipoids.*<sup>51</sup>

The term lipid is one of recent origin; it appears to have been first employed by Overton in 1901 for a group of substances contained in the protoplasm of all cells, especially in their outer layer or cell-membrane. Overton pointed out, in his work on narcotics, that materials which act as anæsthetics (such as ether and chloroform) are capable of obtaining an entry into the cell, because they are soluble in the lipoids of the cell-membrane. Whether this is a correct explanation for the narcotic properties of all drugs or not, the fact which is undoubted is the solubility of many anæsthetics in lipid substances, and the solubility of the lipoids in these anæsthetic reagents. In their solubility in such reagents as ether, chloroform, alcohol, etc., the lipoids resemble the fats and fatty acids; hence their name.

The interest recently bestowed on the lipoids is due, not only to their chemical properties, but also to their biological importance. Although present in smaller amount than proteins, they appear to be essential constituents of protoplasm, and the labile character of their molecules, in many cases, is a property they share in common with the proteins. There seems to be a good deal of truth in the opinion expressed by Bang that the importance of proteins as "carriers of life" (*Träger des Lebens*) has been over-estimated, whilst that of the lipoids has been neglected. The lipoids are contained in special abundance in that tissue, which, above all others,

<sup>51</sup> In the preparation of this section, I have been much helped by two courses of lectures delivered at King's College by O. Rosenheim, who has devoted much of his time to a study of the lipoids. The first of these lecture courses has been published in a condensed form in *Science Progress*, 1908, April and July.

manifests what we still may call "vital properties," namely, the nervous tissues, and it is in the brain and similar structures where they have been most studied. Thudichum's great work on brain chemistry, published in 1874, was very much neglected, probably because of the polemical nature of most of his writings. It was, however, valuable pioneer work, and the research of the last few years has done much to demonstrate its correctness. Many statements, attributed in text-books to more recent investigators, are merely confirmations of what Thudichum discovered. Confusion has been introduced into a subject already sufficiently complex by the coining of many names for the same substances. I shall endeavour here to retain, as far as possible, Thudichum's original nomenclature, and although Thudichum did not employ the term lipid, his classification of them is still the one which is adopted.

The lipids are practically all contained mixed with fat, fatty acids, and lipochromes in the ether-alcohol extract of tissues and organs. Their separation from the fats, and from each other, is usually difficult, involving troublesome processes of fractional precipitation by various solvents, into a description of which I do not intend to enter. Selective extraction, however, is sometimes possible, and gives much better results; for instance, if the residue of the alcohol-ether extract is treated with cold acetone, cholesterol only passes into solution; if extraction with hot acetone is then performed, the mixture known as protagon is extracted; and protagon may be separated into its constituents by pyridine and so forth.

The lipids may be classified in the following way:

1. Those which are free from both nitrogen and phosphorus. The most important member of this group is cholesterol.

2. Those which are free from phosphorus, but contain nitrogen. These yield galactose on cleavage, and were termed cerebrogalactosides or cerebrosides (for short) by Thudichum. Phrenosin and kersasin are the best known members of this group.

3. Those which contain both phosphorus and nitrogen; and which are best known by Thudichum's name of phosphatides. They are grouped by Erlandsen<sup>52</sup> according to the proportion of nitrogen and phosphorus in their molecules as follows:

a. Monoamino-monophosphatides,  $N : P = 1 : 1$ , for instance, lecithin and kephalin.

b. Diamino-monophosphatides,  $N : P = 2 : 1$ , for instance, sphingo-myelin and amido-myelin.

c. Monoamino-diphosphatides,  $N : P = 1 : 2$ , for instance, cuorin of heart muscle.

<sup>52</sup> *Ann. Report*, 1907, 251.

d. Diamino-diphosphatides,  $N:P=2:2$ . One of these was separated from brain by Thudichum, but has not since been examined.

e. Triamino-monophosphatides,  $N:P=3:1$ . One of these (neottin) is present in egg-yolk. It differs from other phosphatides in yielding no unsaturated fatty acids.

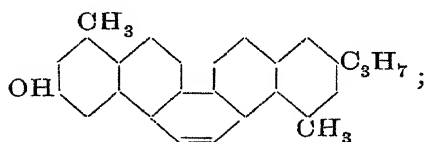
This system of classification is obviously capable of extension, as phosphatides are discovered in which the  $N:P$  ratio is different from those enumerated above

We may now take these various substances in order, mentioning in relation to each the new facts which have been made out concerning them during the last year.

*Cholesterol*.—This is found in small quantities in all forms of protoplasm; until within the last month it was stated to be absent, however, in heart muscle. J. A. Gardner<sup>53</sup> has reinvestigated this point, and finds it present there in about the same proportion as in other forms of muscular tissue. It is a specially abundant constituent of nervous tissues, particularly in the white sheath of nerve fibres. It occurs there in the free state, and is readily extracted by cold acetone.

Until a few years ago all that was known of its chemistry was that it has the formula  $C_{27}H_{44}O$  (or  $C_{27}H_{46}O$ ), and that it is an unsaturated monatomic alcohol.

Recent research has shown that it belongs to the terpene family, a group of substances previously known only in plants, and the following formula has been tentatively put forward to indicate its constitution:



that is, five reduced benzene rings are linked together, and it is important to note that in order that cholesterol may exercise its physiological action, the double linking shown as well as the hydroxyl group must be intact.<sup>54</sup>

Cholesterol compounds also exhibit a physical phenomenon

<sup>53</sup> Communication made to the Physiological Society, December, 1908: not yet published. C. Dorée (*Proc. physiol. Soc.*, 1908, lviii—lix; *J. Physiol.*, **37**; *A.*, ii, 769) has also found cholesterol in coelenterate animals.

<sup>54</sup> The function of cholesterol in enabling the body cells to withstand the action of toxins was indicated in last year's Report (pp. 252—253). A very useful summary of the chemistry, distribution, and biological importance of the cholesterols and phytosterols (vegetable cholesterols), with bibliographical references, is given in an article by W. Glikin (*Biochem. Zentr.*, 1908, **7**, 289, 351).

recently studied by Lehmann, namely, the formation of liquid crystals, which is also given by several other lipoids. It is not within the province of this article to enter into the many interesting data which the study of liquid crystals has brought out; it will be sufficient for my present purpose to point out two only of these, both having a biological bearing.

The first of these relates to what Virchow termed "myelin-forms" in 1855. If brain substance is mixed with water, threads are observed shooting out and twisting into fantastic shapes; these have a superficial resemblance to nerve fibres, and the movements often simulate protoplasmic or amoeboid movements. The term "myelin-forms" applied to them is somewhat unfortunate, for the word myelin has been applied to different chemical substances, and it has now no precise chemical meaning; it is most frequently employed synonymously with the white sheath of nerve fibres, and no doubt the earlier observers thought that myelin-forms were associated in some way with the behaviour of the lecithin-like substances which are present in white matter. Myelin-forms can also be obtained with cholesterol mixtures, and some have gone so far as to say, "without cholesterol no myelin-forms." This is not correct, for other lipoids and also certain oleates show the same phenomenon. Various theories have been advanced to account for myelin-forms, and some of these imply that in the investigation of this remarkable appearance will be found the explanation of living movement. It has now, however, been conclusively shown that myelin-forms are merely distorted liquid crystals, due to the presence of cholesterol and other lipoids.

The second biological outcome of a study of liquid crystals relates to the fat globules seen in the cortex of the suprarenal body, during cell-proliferation in cancer, and in the liver and other organs during so-called fatty degeneration. These are not composed of fat, for the polarisation microscope shows them to be anisotropic, and further investigation has shown them to be lipoids in the fluid crystalline condition.<sup>55</sup> There is no doubt that cholesterol forms a very considerable constituent of these globules, but it was found that pure cholesterol, or cholesterol ethers, do not exhibit the phenomenon, nor do they give the characteristic colour reactions which are given by the white matter of nerve fibres. What appears to be necessary is a mixture of cholesterol and fatty acid, and it has been suggested that in such mixtures the acid is incorporated as "acid of crystallisation," analogous to the "water of

<sup>55</sup> C. P. White, *J. Path. Bact.*, 1908, **13**, 3, 11; J. L. Smith and others *ibid.* 14; *A.*, ii, 966, 968, 972; T. Panzer, *Zeitsch. physiol. Chem.*, 1907, **54**, 239; *A.*, ii, 122.

crystallisation" in many other crystals. It is quite probable that the ethers of cholesterol described by Hürthle as present in the blood are not true esters, but similar mixtures of cholesterol and fatty acid. This is rendered all the more probable if the view that cholesterol is a protective agent against toxins is upheld; for we have already seen that, in order that it may exercise this function, the double linking and the hydroxyl group must be intact, which would not be the case in an ether. We have already noted that cholesterol occurs free in the brain, and Salkowski has shown that the same is true for the cholesterol of the bile.<sup>56</sup>

The globules referred to, however, do not consist altogether of cholesterol mixtures. Rosenheim and Miss Tebb have prepared from the suprarenal cortex a substance analogous to the sphingomyelin of brain which shows the same appearances.<sup>57</sup>

These investigations throw light on the possible function of the cortex of the suprarenal gland; it may be that the cells there are engaged in the secretion of cholesterol and other lipoids, and that this has some connexion with the regulation of growth and development; from his observations on the liquid crystals of tumours, C. P. White<sup>58</sup> suggests that cholesterol is associated rather with cell-proliferation than cell-degeneration; and Mendel,<sup>59</sup> in his studies on growth in embryos, arrives at much the same conclusions; in the chick embryo, cholesterol disappears like the other lipoids of the yolk, being sources of energy in growth.

Before passing from cholesterol to the consideration of other lipoids, there is one more piece of work which deserves a passing reference; I refer to that by C. Dorée and J. A. Gardner<sup>60</sup> on the excretion of cholesterol. At an earlier date, when cholesterol was supposed to be a mere waste material excreted by the bile, Austin Flint found in the fæces a substance which he named stercorin, and which, as he rightly surmised, is a cholesterol derivative. This material, which was re-named coprosterol by Bondzynski, is a saturated alcohol with the formula  $C_{27}H_{48}O$ ; its presence in the fæces is, however, not constant; it was found by Dorée and Gardner in dogs' fæces after feeding on raw brain, but in dogs fed on cooked vegetables or meat, cholesterol is present as such. Whether this cholesterol originates from the food or from the bile is very uncertain, for in horses it is entirely absent; if these animals excrete cholesterol in their bile, it must therefore either be destroyed or re-absorbed. The substance called hippo-

<sup>56</sup> *Zeitsch. physiol. Chem.*, 1908, **57**, 521, *A.*, ii, 1055.

<sup>57</sup> *J. Physiol.*, 1908, **37**, 348; *A.*, ii, 879.

<sup>58</sup> *J. Path. Bact.*, 1908, **13**, 3; *A.*, ii, 972.

<sup>59</sup> *Amer. J. Physiol.*, 1908, **21**, 77; *A.*, ii, 208.

<sup>60</sup> *Proc. Roy. Soc.*, 1908, **80**, B, 212, 227; *A.*, ii, 514.



coprosterol in horses' fæces (which was formerly supposed to be analogous to coprosterol of human or dogs' fæces, and considered to be derived from the bile by bacterial reduction in the intestine) is only present after feeding on grass, and is undoubtedly a phytosterol or cholesterol of vegetable origin. Following the usual custom of labelling phytosterols by their plants of origin, Doré and Gardner propose to term it chortosterol to indicate that it is derived from grass; its formula is  $C_{27}H_{54}O$ , and it gives none of the usual colour reactions of cholesterol.

The only paper I shall allude to on the protective action of cholesterol confirms those I referred to in last year's Report. It is by Minz,<sup>61</sup> and deals with cobra and viper venoms. Cobra venom, as is well known, contains two toxins, one which dissolves blood-corpuscles (hæmolysin), and the other which attacks nerve-cells (neurotoxin); the hæmolytic action of the venom is alone inhibited by cholesterol; the latter is believed to remove from solution the lecithide, the prolecithide, and to a less degree lecithin itself. It will be seen from this that the author accepts the statements of Kyes and others concerning the part lecithin and lecithides play in the anchoring of toxins on to cells, statements which we shall presently see have been subjected to criticism. The action of the neurotoxin is not influenced by cholesterol. Viper poison also contains two toxins, a hæmolysin, and a poison which leads to the occurrence of hæmorrhages (hæmorrhagin). The latter is not inhibited by cholesterol, the former is. The hæmorrhagin, however, is destroyed by hydrochloric acid, the hæmolysin not.

*The Cerebrosides.*—A warm alcoholic extract of brain deposits a white precipitate on cooling; if the cholesterol contained in this deposit is extracted with ether, the residue may still be called protagon, not as implying that it is a definite chemical individual, but as a convenient expression, employed in much the same way as the term peptone is still used for a mixture of protein cleavage products. Protagon was originally called *cèrèbrote* by Couerbe; the word protagon we owe to Liebreich, who regarded it not only as a definite compound, but the mother substance of the other phosphorised and non-phosphorised constituents of nervous tissue. It has now been conclusively proved in confirmation of what Thudichum stated in 1874, that protagon is a mixture of phosphorised and non-phosphorised substances, in such proportions that it usually contains about 1 per cent. of phosphorus.<sup>62</sup>

<sup>61</sup> *Biochem. Zeitsch.*, 1908, 9, 357; *A.*, ii, 413.

<sup>62</sup> The attempted resuscitation of protagon by Cramer alluded to in last year's Report (pp. 247—249) has led to further writing of a somewhat polemical nature

By treatment with appropriate reagents and recrystallisation, protagon can be separated into its constituents; the best method is to dissolve "protagon" in pyridine; on allowing this solution to stand, the constituent rich in phosphorus separates out in the form of anisotropic globules (fluid sphæro-crystals), and those which are free from phosphorus and comprise about 70 per cent. of the original protagon remain in solution. The phosphorus-rich constituent is a phosphatide sphingo-myelin which we shall deal with under its appropriate heading, and the phosphorus-free constituents are the cerebrosides. Although these have received many names, the total number of known cerebrosides is two. These are named, to employ Thudichum's original terminology, phrenosin and kerasin. The former is a crystalline product, the latter of waxy consistency.

Phrenosin yields on cleavage three substances:-

(1) A reducing sugar, galactose.

(2) A base termed sphingosine, about which little or nothing chemically is yet known

(3) A fatty acid, termed neuro-stearic acid by Thudichum; it has a higher molecular weight than stearic acid, but has not been yet definitely identified.

Kerasin also yields galactose and sphingosine, but its third constituent, the fatty acid, is not neuro-stearic, but another acid, which has also not been identified as yet.

The only noteworthy piece of work during the last year relating to these substances is that by K. Takaki<sup>63</sup> in connexion with phrenosin, which he speaks of under Thierfelder's name as cerebron. He finds that it is one of the substances in the brain which unites with tetanus toxin; it is apparently not the only brain constituent which acts in this way, for more of the tetanus toxin disappears when mixed with brain substance than can be accounted for by that which combines with the phrenosin. It is apparently the neuro-stearic acid constituent of phrenosin which is responsible for this action.

### *The Phosphatides.*

We are now free to pass to a consideration of the phosphatides, and will deal with them under the headings already given in our classification a few pages back. In the first group, the mono-

(see Wilson and Cramer, *Quart. J. exp. Physiol.*, 1908, 1, 97; *A.*, i, 234; Rosenheim and Miss Tebb, *ibid.*, 297; also *J. Physiol.*, 1908, 37, 341, 348; *A.*, ii, 879). The additional facts brought out by the last-named observers will, it is to be hoped, be successful in "laying" protagon beyond hope of further resurrection.

<sup>63</sup> *Beitr. chem. Physiol. Path.*, 1908, 11, 288; *A.*, ii, 521.

amino-monophosphatides, we have to deal with lecithin and kephalin.

*Lecithin*—Although the empirical, and probably also the constitutional, formula of this substance are fairly well known, such knowledge is largely based on conjecture, for lecithin is a most labile material, as recent work on its cadmium and other salts has shown.<sup>64</sup> We know, however, that on decomposition it yields the base choline, glycerophosphoric acid, and two fatty acid radicles. The nature of the fatty acids may vary, but in the lecithins found in the body, oleic acid is always one; the fatty acid radicles are linked to glycerol as they are in ordinary fats. The place of the third fatty acid radicle of an ordinary fat is taken by the phosphoric acid radicle, and this in its turn is in ethereal combination with choline.

Lecithin forms compounds with many substances, with metals, with alkaloids, with proteins (lecitho-proteins), and with carbohydrates. Possibly many of these are adsorption rather than true compounds.

The main interest of lecithin to the biologist is the part it is supposed to play as an amboceptor in linking poisonous proteins to cell protoplasm, as was first pointed out by Kyes in his work on the hæmolysin of cobra venom.<sup>65</sup> I accepted this view with considerable reserve in my Report last year, and my cautiousness has been justified by much of the work that has been issued during the current twelve months. If teleological argument is permissible, it is difficult to see the advantage in the struggle for existence which lecithin would confer upon living organisms. It may, of course, be that the assimilation of a food protein is on all fours with that of a toxic protein, and the nutritive value of lecithin, which has been asserted so frequently, may possibly rest upon this among other factors; but even this falls to the ground if the assimilation of protein matter is usually accomplished, not by the incorporation of ready-made protein, but by that of its simple (amino-acid) cleavage products.

I. Bang, who stands in the front rank of modern investigators, in his attempts to repeat the work of Kyes, has entirely failed to substantiate his main premises.<sup>66</sup> He finds that the existence of cobra lecithide is unproved, and that Kyes's lecithides are mixtures of fats, soaps, and decomposition products of lecithin. Lecithin itself is wholly inactive as an activator; the same is true for cuorin. He found the kephalin fraction to possess some activity

<sup>64</sup> W. Heubner, *Arch. exp. Path. Pharm.*, 1908, 59, 420; *A.*, 1909, i, 5.

<sup>65</sup> *Ann. Report*, 1907, 251.

<sup>66</sup> *Biochem. Zeitsch.*, 1908, 11, 520; *A.*, ii, 721.

in this direction, but there was no guarantee even here that he was dealing with a pure substance, and he found that Kossel's 'protagon' (which he speaks of incorrectly as consisting largely of kephalin) is also inactive. What does seem to be certain is that the hæmolysis produced by snake venom depends on the existence of a lipolytic enzyme; this view is accentuated by the careful work of v. Dungern and Coca.<sup>67</sup> It is the scission products liberated by such an enzyme which act hæmolytically, especially de-oleo-lecithin (that is, lecithin minus its oleic acid) and oleic acid itself. These observers agree with Bang that compounds of lecithin and cobra toxin do not exist, and that Kyes's preparations are mixtures of numerous substances. Cobra poison contains no amboceptor, and the hæmolysis produced by a combination of cobra poison and the complement of serum is due to a complex serum hæmolysin which acts only in certain circumstances, of which the most important is that the blood-corpuscles must have taken up a certain quantity of lipase.

In this connexion it should also be noted that the Wassermann reaction of the cerebro-spinal fluid so much employed to-day for the detection of syphilis is also due to lipolytic activity, probably produced by the agency of the syphilis parasite (spirochæte).

Two papers deal with the estimation of lecithin in animal tissues; one of these is by W. Glikin,<sup>68</sup> who finds a specially high percentage of this substance in the bone-marrow of new-born animals, especially in those which are born in an immature condition. The other is by J. Nerking,<sup>69</sup> who has estimated the total yield in the bodies of certain animals, as well as in their individual organs. In the rabbit the quantity works out as 0.4 per cent. of the body-weight. In the hedgehog the yield is especially high, particularly in bone-marrow and suprarenal. Nerking somewhat inconsequently concludes that this may explain the comparative immunity the hedgehog possesses against snake-bite; for if lecithin favours the safe anchorage of snake poison, it can hardly be expected to act also as a protection against the venom. The hedgehog, if immune against snakes, much more probably owes its freedom from attack to its protective coating of spines.

*Choline.*—This basic product of lecithin cleavage possesses a good deal of physiological interest; its presence in the circulating fluids is an exact chemical proof of the breakdown of lecithin, and so of nervous material. The methods of detecting this substance I need not go into again, but will refer readers interested in the

<sup>67</sup> *Biochem. Zeitsch.*, 1908, 12, 407; *A.*, ii, 866.

<sup>68</sup> *Ibid.*, 1907, 7, 286; *A.*, ii, 120.

<sup>69</sup> *Ibid.*, 1908, 10, 193; *A.*, ii, 608.

subject once more to my Report of last year. Choline does not pass as such into the urine; therefore if this test for nervous degeneration is employed, the patient must be prepared to sacrifice a small quantity either of his blood or cerebro-spinal fluid. The examination of the urine does, however, give some indication of nervous breakdown (in the actual, not the figurative, sense), for Bauer<sup>70</sup> has shown that the trimethylamine of the urine is considerably increased in such circumstances. This product of lecithin degradation is also increased by the administration of foods rich in lecithin. It is not increased if the nervous disease is functional (that is, figurative rather than actual).

A few years ago Donath stated that choline is discoverable, at any rate, in one disease, usually reckoned as functional, namely, epilepsy. Kajiura<sup>71</sup> in my laboratory has shown that this is not so, and has pointed out how Donath made his mistake.

H. MacLean<sup>72</sup> finds that only 52 per cent. of the nitrogen of lecithin is recoverable in the choline. He therefore suggests that another nitrogenous base may be present in lecithin; or, of course, it is possible that his method for the collection of the choline was not sufficiently accurate.

C. Schwarz and R. Lederer<sup>73</sup> identify the substance that lowers blood-pressure in extracts of the thymus, spleen, and lymphatic glands, as choline; v. Fürth and Schwarz<sup>74</sup> find the same true for the depressor substance in thyroid extracts; and the same observers<sup>75</sup> have also stated that the secretin of Bayliss and Starling contains considerable quantities of choline. Choline produces a flow of pancreatic juice, but it is not identical with secretin, the action of secretin on the pancreatic flow being only partly neutralised by atropine, whilst that of choline is wholly inhibited by the same alkaloid.

Speaking of the antagonisms of choline leads me next to mention an investigation by A. Lohmann,<sup>76</sup> who finds that adrenaline and choline are antagonistic so far as relates to blood-pressure, cardiac activity, and intestinal peristalsis, but not in relation to the diabetic condition which adrenaline sets up.

The foregoing mention of secretin leads me into another parenthesis, and a reference to a polemical paper by L. Popielski.<sup>77</sup> He still considers that pancreatic secretion is largely influenced

<sup>70</sup> *Beitr. chem. Physiol. Path.*, 1908, **10**, 502; *A.*, ii, 717.

<sup>71</sup> *Quart. J. exp. Physiol.*, 1908, **1**, 291; *A.*, 1909, ii, 71.

<sup>72</sup> *Zeitsch. physiol. Chem.*, 1908, **57**, 296; *A.*, ii, 967.

<sup>73</sup> *Pflüger's Archiv*, 1908, **124**, 353; *A.*, ii, 968.

<sup>74</sup> *Ibid.*, 361; *A.*, ii, 968.

<sup>75</sup> *Ibid.*, 427; *A.*, ii, 963.

<sup>76</sup> *Ibid.*, 1908, **122**, 203; *A.*, ii, 407.

<sup>77</sup> *Ibid.*, 1907, **120**, 451; *A.*, ii, 119.

by nervous reflexes; he finds that extracts of all parts of the gastro-intestinal mucous membrane produce the effects of "so-called secretin," and is not limited to the upper portion of the intestines. He also calls Bayliss and Starling to book for labelling, with a chemical name, a substance of which they know nothing chemically. This is a piece of good advice which he unfortunately forgot to apply to his own work a few months later, when he named the unknown substance in Witte's peptone which lowers blood-pressure, vaso-dilatin.<sup>78</sup>

A somewhat lengthy communication on the physiological action of choline by G. Modrakowski<sup>79</sup> must next be referred to; he finds that this substance, prepared synthetically, does not, when absolutely pure, produce lowering of blood-pressure, as all previous observers have found. On the contrary, it raises blood-pressure. This, however, does not invalidate the work of those who have used the depressor effect usually seen as a physiological test for choline, for extraordinary precautions have to be taken to prevent the pure choline from undergoing that change which leads to the development of a depressor modification. The impurity or modification which causes the fall of blood-pressure is also considered to be responsible for some other physiological effects previously ascribed to choline; it is neutralised by atropine, and that, according to Modrakowski's view, is the reason why even impure choline will produce a rise in blood-pressure after an animal has been atropinised.

*Kephalin*.—This is a monoamino-monophosphatide, concerning which we know much less than we do of lecithin. If an ethereal extract of brain is evaporated and the residue treated with alcohol, lecithin enters into solution, but kephalin remains undissolved. Its name indicates the waxy nature of this compound. On decomposition, it yields phosphoric acid, and fatty acids which are less saturated than oleic and probably belong to the linoleic series. It is questionable whether the base it contains is choline. It is found also in egg-yolk, and appears to be the most abundant phosphatide in nerve fibres, and that this is contained not merely in the medullary sheath is seen by comparing the figures for medullated and non-medullated fibres. F. Falk<sup>80</sup> gives the following numbers:

	Medullated nerve.	Non-medullated nerve.
Cholesterol ..	25.0 per cent.	47.0 per cent.
Kephalin ..	12.4 "	23.7 "
Cerebrosides ..	18.2 "	6.0 "
Lecithin ..	2.9 "	9.8 "

<sup>78</sup> *Arch. exp. Path. Pharm., Suppl.*, 1908, 435; *A.*, ii, 1059.

<sup>79</sup> *Pflüger's Archiv*, 1908, 124, 601; *A.*, ii, 974.

<sup>80</sup> *Biochem. Zeitsch.*, 1908, 13, 153; *A.*, ii, 965.

Under the heading of the second group of phosphatides, in which the N: P ratio is 2: 1, we have to consider two substances, namely, sphingo-myelin and amido-myelin.

*Sphingo-myelin* was the name well selected by Thudichum for this material, on account of its sphinx-like character. It is the constituent of so-called protagon which contains the phosphorus, and it is the one which is slowly deposited from a solution of protagon in pyridine. It resembles lecithin in yielding choline on cleavage, but differs, among other points, from the phosphatides already mentioned in yielding no glycerol on decomposition. The nature of the alcohol which takes the place of glycerol is uncertain. It may also be prepared from the cortex of the suprarenal body, and exhibits a physical phenomenon which has hitherto not been described in connexion with any other substance; this was discovered by Rosenheim and Miss Tebb<sup>81</sup> during their work on the optical activity of protagon.

"Protagon," dissolved in pyridine, possesses at 30° a slight dextrorotatory power, which changes to optical inactivity at higher or lower temperatures, showing a maximum lævorotation of  $-242^{\circ}$  and a final constant lævorotation of  $[\alpha]_D^{20} -13.3^{\circ}$ . Wilson and Cramer had also noticed the constancy of this figure, although they omitted to note the change of sign, and they took this constant as one of their proofs for the chemical entity of protagon. The explanation of the change is as follows: When a solution of "protagon" in pyridine is kept at 20°, sphingo-myelin is precipitated, and it is the appearance of this precipitate of fluid sphærocrystals which gives rise to the high lævorotation; as the precipitate settles, the lævorotation decreases, and the final lævorotation is due to a minute quantity of the precipitate which does not settle. But if the precipitate is removed by filtration or centrifugation, the fluid (which then contains the cerebrosides only) is optically inactive. If the precipitate is once more shaken up with the fluid, high lævorotation is again obtained, which lessens as the precipitate once more settles. This is the first time optical action of this nature has been observed in substances not actually in solution, and the term sphærorotation is proposed for the phenomenon. Although these observers express the high lævorotation in the usual way, the optical activity of the precipitated material does not follow Biot's laws.

*Amido-myelin*.—This is another monoamino-diphosphatide described by Thudichum which has not been examined since his time. It possesses the protein-like character of being coagulable by heat.

<sup>81</sup> *J. Physiol.*, 1908, **37**, 348; *A.*, ii, 879.

The third group of the phosphatides contains those in which the N : P ratio is 1 : 2. The best known of these is *cuorin*. This substance received its name from Erlandsen,<sup>82</sup> who first found it among the phosphatides of heart muscle, but it has since been found in liver and other organs, and also (or a corresponding monoamino-diphosphatide) in egg-yolk.<sup>83</sup> On decomposition it yields glycerol, fatty acids, and a base, but the nature of these last-named constituents has not yet been made out.

The remaining groups of the phosphatides we know still less about, and beyond their enumeration already given in the classification on p. 230, there is practically nothing to say about them. There is, however, one more substance which we must mention in order to make our survey complete, and this is *jecorin*. With a brief description of this substance, our account of the lipoids may be brought to a conclusion.

*Jecorin*.—This material was originally so named by its discoverer, Drechsel, who found it first in the liver, and later in other organs. Much doubt has been expressed concerning its chemical individuality; the yield of sugar from it was found to be inconstant, and it has therefore been very generally regarded as one of numerous adsorption or similar compounds of lecithin and sugar, the proportion between which varies with the amount of sugar in the organ it is obtained from. The recent work of Baskoff<sup>84</sup> has, however, shown that by a careful method of preparation it is possible to obtain a product of constant composition yielding 14 per cent. of sugar and a considerable quantity of incorporated ash. He has further shown that the phosphatide in combination with the sugar is not lecithin, but a member of the diamino-monophosphatide group.

It was my intention, on starting this Report, to conclude it with an account of recent work on the pituitary body. I find now that I have already overstepped the limits of the space allotted to me, and so I propose to postpone the consideration of this interesting gland to my next Report. The work in relation to this subject is still unfinished, so there may be a more complete story to tell this time next year.

W. D. HALLIBURTON.

<sup>82</sup> *A.*, 1907, i, 371.

<sup>83</sup> H. MacLean, *Zetsch. physiol. Chem.*, 1908, 57, 304; *A.*, ii, 963.

<sup>84</sup> *Zetsch. physiol. Chem.*, 1908, 57, 395; *A.*, i, 1029.



## AGRICULTURAL CHEMISTRY AND VEGETABLE PHYSIOLOGY.

DURING the past year the activity of the many workers in this very varied field, which includes the chemistry of the soil and of the nutrition of both plants and animals, has been well maintained, although nothing very novel has come to light either in the way of a discovery or a new point of view. We are advancing towards an analysis and a reconstruction of all the varying play of forces involved in the growth of a plant from seed round to seed again, but in reviewing the progress effected during a year one is more conscious of the flight of time than of the lessened distance to the goal. Very often, indeed, a large proportion of the work seems to be devoted to the undoing of previous investigations, but the conditions under which a plant grows are so complex, and its development represents the resultant of so many different actions, that investigations which seem to lead to definite conclusions in the laboratory are apt to be true only for that particular set of circumstances, and to have only a limited application to the open field, where the results may be determined by some other factor not taken into account in the experimental work.

### *Soil Bacteriology.*

In connexion with the bacteriology of the soil, attention is still mainly directed to the question of nitrogen-fixation, for although the main facts are not in doubt, there are considerable differences of opinion as to the magnitude of the part played by the different races of nitrogen-fixing bacteria in Nature.

As regards *Azotobacter chroococcum*, the most active of the bacteria which fix nitrogen when free in the soil, its original discoverer, M. W. Beyerinck,<sup>1</sup> has abandoned the idea, which he once put forward, that the actual fixation is effected by another organism, *Radiobacter*, living in symbiosis with *Azotobacter*; he now agrees with the many other observers, who kept to his original opinion, that *Azotobacter* is the effective agent. Beyerinck suggests

<sup>1</sup> *Proc. K. Akad. Wetensch. Amsterdam*, 1908, 11, 67; *A.*, ii, 975.

the use of calcium malate, instead of mannitol or glucose, in the culture media used for identifying the presence of *Azotobacter* in samples of soil, because a larger number of organisms develop into colonies on this medium than on the more usual ones containing sugar. He also makes the interesting statement that colonies of *Azotobacter* seem to be associated with the roots of leguminous plants even when they are not abundant in the rest of the soil, an observation which requires careful examination to see if this association is confined to leguminous plants. Krzemieniewski<sup>2</sup> explains the superior nitrogen-fixation per gram of sugar oxidised which is found when the inoculation is made with a raw soil extract instead of a pure culture of *Azotobacter*, as due to the small quantity of soluble humate that is added with the soil extract. It was found that pure cultures of *Azotobacter* could be stimulated to a much greater fixation by the addition of a little sodium or potassium humate. On the other hand, Löhnis and Pillai<sup>3</sup> conclude that humus alone is about the least effective source of carbon for the *Azotobacter* organism, mannitol and xylose being most effective; dextrose, starch, sodium tartrate, calcium lactate, sodium propionate are successively lower down in the scale. These authors also give a series of measurements of the activity of the organism in soils that have received different manurial treatment, and in the same soil at different times of the year; but their results are not very convincing, probably because their method of determining the activity of the soil was not satisfactory. Among the chief *desiderata* in connexion with soil bacteriology are satisfactory methods for measuring the power of a given sample of soil to bring about certain kinds of bacterial action, for example, nitrogen-fixation, nitrification, production of ammonia, protein fission, etc.; for none of those which have been hitherto proposed seem to give results in accord with the field experience. Stoklasa and his co-workers<sup>4</sup> have also discussed the relationship of *Radiobacter* to *Azotobacter*, and find the former of little value as a nitrogen fixer; they, too, have compared the various sugars as sources of carbon for *Azotobacter*, and state that *l*-arabinose is the most effective, and that all the other monosaccharides possess much the same value, considerably above that of the disaccharides. The same workers have been studying the chemical reactions involved in the fixation of nitrogen; they found that from dextrose the chief product was carbon dioxide, but ethyl alcohol, formic, lactic, and acetic acids were also produced, and some hydrogen was always liberated. Stoklasa is

<sup>2</sup> *Bull. Acad. Sci. Cracow*, 1907, 746.

<sup>3</sup> *Centr. Bakt. Par.*, 1908, ii, 20, 781; *A.*, ii, 522.

<sup>4</sup> *Ibid.*, 21, 484, 620; *A.*, ii, 880, 975.

very positive above the hydrogen and the ethyl alcohol, the formation of which other observers have denied; but in all probability the reaction varies with the source and the activity of the particular culture of *Azotobacter* employed.

The magnitude of the part played by *Azotobacter* in Nature is still a matter of uncertainty. J. G. Lipman<sup>5</sup> has made a number of inoculation experiments with soil treated in various ways, but without any very positive results to show that the *Azotobacter* had succeeded in fixing enough nitrogen to affect the yield of the crop afterwards grown in the soil. As this author, however, very soundly points out, the mere inoculation of a given organism into a soil in which it was previously lacking, is never likely to result in its establishment therein, unless at the same time the general soil conditions are made suitable for it. The absence of the organism is in itself most probably an indication that the soil is not a fit medium for its growth, nor can it be established until the inhibiting factors have been removed.

Since the discovery of *Clostridium*, *Azotobacter*, and their related organisms which will fix nitrogen when grown on suitable nitrogen-free media, the power of fixing a little nitrogen has been attributed to a large number of other organisms; indeed, it has been supposed to be a property common to all oxidising bacteria under fitting conditions; Bredemann<sup>6</sup> reports studies on a bacterium only about one-fourth as effective as *Azotobacter*. Fröhlich<sup>7</sup> makes out that certain fungi associated with dead leaves, etc., possess the power, whilst Hannig<sup>8</sup> maintains that a certain grass, when associated with a parasitic fungus on the root, will bring some free nitrogen into combination.

As regards the nitrogen-fixing bacteria associated with leguminous plants, there is nothing new to record; cases continue to be reported where inoculation of the ground with the nodule organism has caused a marked increase in the yield of the crop, but they refer to relatively exceptional soils or crops; under ordinary farming conditions nothing appears to be gained by inoculating the seeds of such staple crops as clover or beans. Reports appear from time to time that the nodule organisms have been made to associate with non-leguminous plants, but no evidence is yet forthcoming.

Nitrification continues to receive some attention; L. C. Coleman<sup>9</sup> has been studying the effect of organic matter, which the early investigators of nitrification had regarded as inhibitory of nitrifica-

<sup>5</sup> 28th Ann. Rep. New Jersey State Agric. Exper. Stat., 1906—1907, 141; *A.*, ii, 615.

<sup>6</sup> *Centr. Bakt. Par.*, 1908, ii, 22, 44.

<sup>7</sup> *Ibid.*, 21, 162.

<sup>8</sup> *Ber. Deut. bot. Ges.*, 1908, ii, 26a, 238; *A.*, ii, 523.

<sup>9</sup> *Centr. Bakt. Par.*, 1908, ii, 20, 401, 484; *A.*, ii, 315.

tion. He found, however, that small quantities of dextrose, up to 0.5 per cent., increased the rate of nitrification in non-sterilised soils, and a similar effect was seen when 0.02 to 0.05 per cent. of dextrose was added to pure cultures. Karpiński and Niklewski<sup>10</sup> obtained similar results with humates and soil extracts, also with sugar and acetates, which latter salt Coleman found injurious to the process. These contradictions, which are always turning up when the nutrition of bacteria is being examined, only emphasise the need for caution in drawing conclusions from laboratory experiments as to the behaviour of soils in the field.

Hall, Miller, and Gimingham<sup>11</sup> have examined the biological condition of some of the Rothamsted soils which have become acid through the repeated application of ammonium sulphate and chloride. In these soils, nitrification is practically at a standstill, and the nitrification organisms are only to be found sparsely, if at all. The authors show that the acidity is mainly due to free humic acid, although a little hydrochloric and sulphuric acids must also be present to a greater extent after the application of the manures than later in the year. The acid arises from the ammonium salts, which are split up by certain micro-fungi and moulds abundant in the soil of these plots, the ammonia being utilised by the fungus and the acid set free. These acids have year by year attacked the calcium humate in the soil and set free humic acid, which, being sparingly soluble, has accumulated. The poor growth to be seen on these acid plots may be put down to the fact that the grasses are driven to draw their nitrogen directly from the ammonium salts without previous nitrification, and generally to the manner in which the acidity of the medium causes the replacement of the normal bacteria in the soil by a fungus flora, which competes with the crop for manure and plant food in the soil.

Hall and Miller<sup>12</sup> have attempted to oxidise by soil bacteria the nitrogen compounds contained in powdered rocks taken from great depths beyond the reach of any weathering processes, chiefly clays which show a considerable proportion of nitrogen. They found that some of this material was convertible by bacteria into nitrates—more than could be accounted for by the ammonia which they also found to be always present in these rocks. The process of nitrification is, however, very slow, and the authors consider that some of the nitrogen compounds in soils may originally have been present in the rock out of which the soil was formed by weathering, being, as it were, in a mineralised condition unavailable for the plant.

<sup>10</sup> *Bull. Acad. Sci. Cracow*, 1907, 596; *A.*, ii, 123.

<sup>11</sup> *Proc. Roy. Soc.*, 1908, 80, B, 196; *A.*, ii, 524. <sup>12</sup> *J. Agric. Sci.*, 1908, 2, 343.

M. C. Potter<sup>13</sup> has isolated an organism from garden soil capable of oxidising amorphous carbon in the form of coal, peat, charcoal, etc., which would seem to indicate that such fossilised organic matter is even more attackable by bacteria than previous observers had supposed.

The question of whether the soil bacteria aid in the solution of such nutrients as tricalcium phosphate has received further attention. Perotti<sup>14</sup> considers that the attack only takes place when the nitrogen compound present in the culture medium is a physiologically acid one, for example, ammonium sulphate, and this would agree with Soderbaum's experiments.<sup>15</sup> Sackett, Patten, and C. W. Brown,<sup>16</sup> however, think that other factors come into play, such as the carbon dioxide excreted by the organism, or the specific acid it will form when supplied with an appropriate source of carbon. Even the potash of leucite is attacked when it is introduced into cultures of acid-producing moulds.<sup>17</sup>

Voorhees, Lipman, and P. E. Brown<sup>18</sup> have examined some of the chemical and bacteriological results of liming the soil, and find that after an application of lime the bacterial activity of the soil, as measured by its power of making ammonia from gelatin or its nitrate content, is considerably increased. In their trials, pure lime was more effective than a magnesian lime made from dolomite, and calcium carbonate was often more effective than either.

### *Soil Chemistry.*

The theory of the action of fertilisers, which we owe to Whitney and his colleagues in the Bureau of Soils of the U.S. Department of Agriculture, has received considerable developments during the year. Briefly, the theory is that each plant excretes during growth certain substances toxic to itself but not to other plants; infertile soils are those in which such substances have accumulated; fertilisers act, not by directly feeding the plant, but by neutralising or otherwise putting out of action the toxic bodies excreted by previous crops. Since last year's Report the point of view seems to have changed somewhat; no further work is reported on what was the prime hypothesis (that the soil water possesses a constant composition which is unaffected by the addition of fertilisers) and instead of excretion from the plant itself, the toxic substances are

<sup>13</sup> *Proc. Roy. Soc.*, 1908, B, **80**, 236; *A*, ii, 524.

<sup>14</sup> *Atti R. Accad. Lincei*, 1908, [v], **17**, i, 448; *A*, ii, 527.

<sup>15</sup> *Landw. Versuchs.-Stat.*, 1908, **68**, 433; *A*, ii, 728.

<sup>16</sup> *Centr. Bakt. Pur.*, 1908, ii, **20**, 688; *A*, ii, 415.

<sup>17</sup> *Grazia and Camiola, Bied. Zentr.*, 1908, **37**, 207; *A*, ii, 415.

<sup>18</sup> *New Jersey State Agric. Exper. Stat. Bull.*, 1907, 210; *A*, ii, 317.



vincing. No actual weights are given, and although we gather that the trials were made in duplicate, the two sets are not given separately; thus we have no means of estimating the experimental error, which we know must be large. Furthermore, a substance may be very toxic in a water culture, where the plant is set to grow in distilled water and nothing else, but there is no guarantee whatever that it will behave in the same way in the soil, which possesses an enormous power of withdrawing organic substances from solution. The substances which Schreiner and Shorey have isolated are of great interest, and open up a new field in the study of the organic matter of the soil, but they demand a good deal more investigation before they can be accepted as the causes of the infertility of the soil. For example, a soil rich in organic matter—the accumulation of previous vegetation—is in most cases extremely fertile; are such soils richer or poorer than the average in these so-called toxins?

In another paper, Schreiner and Reed<sup>20</sup> attempt to show that various bodies used as fertilisers destroy or otherwise mask the toxic action of organic plant poisons on wheat seedlings. The fertilisers employed were sodium nitrate and calcium carbonate, the toxins, coumarin, arbutin, and cinnamic acid, and the method of experiment has already been described. The authors give the following table to show the beneficial action of calcium carbonate.

	No addition.	CaCO <sub>3</sub> added 2000 per million.
Control: distilled water only. ....	100	209
Vanillin 1 per million .....	132	201
"  10  "  .....	126	184
"  25  "  .....	80	183
"  100  "  .....	53	127
"  500  "  .....	25	107

Again no actual results are given by which the experimental error may be checked; the increases seen with 1 and 10 per million of vanillin are set down to the stimulus brought about by small doses of poisons (no case has yet been made out for the general truth of this theory of stimulus), but no explanation is attempted of the fact that calcium carbonate added to the pure distilled water in the control experiment increased the growth from 100 to 209. By parity of reasoning, the distilled water must have been the toxin in this case.

Schreiner and Sullivan<sup>21</sup> claim to have extracted from "wheat-sick" soil a substance toxic to wheat, and from "cow pea-sick" soil a substance toxic to cow peas, although not to wheat, but no details are yet given.

<sup>20</sup> *J. Amer. Chem. Soc.*, 1908, **30**, 85; *A.*, ii, 420.

<sup>21</sup> *J. Biol. Chem.*, 1907, **4**, xxvi; *A.*, ii, 422.

We have dealt with these papers at some length because it is only by close attention to the details that they can be judged; each of the papers which emanates from the Washington Division of Soils begins with a convinced exposition of the theory to be proved, and the reader does not always see that the experiments which follow, although they will agree with the theory, are very far from a demonstration of its truth.

If the American authors of the theory seem to be weakening on their original hypothesis that the plants excrete the toxins, their old view has found an independent supporter in India. F. Fletcher<sup>22</sup> was led by certain considerations as to the vigour of the plants in the outside rows of experimental plots, the well-known "fallow effect," to regard this increased growth as due to the comparative freedom of their roots from toxins excreted by neighbouring plants. He then proceeded to make water cultures with certain plants, cotton, sorghum, etc.; he grew young seedlings in well-water for twenty-one days, three times in succession in the same liquid, the volume being kept constant by fresh additions of water. Finally, the solutions thus obtained were allowed to evaporate in a room until in each case about 20 litres of original well-water were reduced to something between 1 and 2 litres. Into these liquids fresh seedling plants were put to grow, but were found to wither and die very quickly, a result the author sets down to the concentrated toxic excretion. On this part of the work certain criticisms suggest themselves—the plants grown in the solutions were really large germinating seeds, in the stage, therefore, of breaking down the protein and other reserve materials contained in the seed. It is well known that the roots of such young seedlings will part with soluble nitrogenous and other compounds to any solution in which they are growing, but one must not argue from the germinating seedling to the normal growing plant, which, as a rule, has not such an excess of nitrogen as to be able to waste any in excretions. Moreover, these water cultures were made in broad, flat vessels, and were allowed to concentrate by standing in a room at an Indian temperature; in what sort of a bacterial condition were they likely to be at the end, and what products may not have been formed! There is some indication that the toxicity of the solutions followed the size of the germinating seeds utilised in each case, but data are lacking. Again, well-water, concentrated to one-tenth of its volume without any check against bacteria, may itself provide something toxic, and it is significant that the worst results were obtained in the case where 23 volumes of well-water were concentrated into one for

<sup>22</sup> *Mem. Dept. Agric. India, Bot. Ser.*, 1908, 2, No. 3; *A.*, ii, 617.



the final test. Other difficulties could be raised, but these will be enough to show that the author subjected his results to no critical examination; it seems a property of this toxin hypothesis that its holders set out with the theory and are content if their experiments will fit, without risking any crucial experiments to try whether they will fit that theory only and no other.

Fletcher considers that his results show all crops to yield the same toxin; he gives a number of reactions which the substance shows, for example, it is precipitated by potassium hydroxide, sodium chloride, dilute sulphuric acid, among other reagents, but in view of the very doubtful origin of the material it is perhaps hardly worth while considering what these reactions indicate.

S. U. Pickering<sup>23</sup> has also entered the "soil toxins" field of discussion with a series of experiments showing that many seeds germinate more slowly in soil that has been heated, the "incubation" period increasing with the temperature from 60° to 150°. In general, the percentage germination also diminishes with the temperature. The soils are shown to contain more soluble matter, both organic and inorganic, after heating, and it is to this increase in the soluble nitrogenous matter by heating that Pickering attributes his results. He concludes that most soils contain substances favourable to germination which are converted into inhibitory substances on heating, although some soils probably contain inhibitory substances at starting. Pickering also considers that this increase of soluble nitrogenous bodies accounts for the results obtained by Darbishire and Russell,<sup>24</sup> who found that the growth of plants is much increased by a preliminary heating of the soil, in which case the substances which retard germination either become destroyed before plant growth begins or have no necessary connexion with it. Pickering dismisses soil bacteria as an effective agency either in his own or in Darbishire and Russell's results, but his original experimental figures seem to form too slender a foundation for the wide conclusions he draws from them.

### *Soil Physics.*

This branch of the subject is still sadly neglected, although it is recognised that both the soil flora and the nutrition of the plant are determined more by the movements of water and air in the soil than by any other single factor; during the year, however, one or two interesting papers have appeared. F. J. Alway<sup>25</sup> has made measurements of the soil moisture in the semi-arid "great plains" regions of Saskatchewan and the North-West. He obtained

<sup>23</sup> *J. Agric. Sci.*, 1908, 2, 411.

<sup>24</sup> *Ann. Report*, 1907, 265.

<sup>25</sup> *J. Agric. Sci.*, 1908, 2, 333.

samples, by means of an auger, down to the depth of six feet from land which had been cropped and from adjacent land which had been fallowed in order to accumulate the rainfall for a crop in the succeeding season. By determining the hygroscopic moisture of each sample, that is, the amount absorbed by the dry soil from a saturated atmosphere, and regarding the difference between this and the actual water in the soil when sampled as the "free" water which would be available for a crop, the author claims to be able to decide, at the commencement of a season, whether the land contains sufficient water for the needs of a crop. The author incidentally denies that the soil in this region is frozen permanently, or that its gradual thawing throughout the growing season keeps the crop supplied with moisture. Alway's figures would seem to indicate that the crop chiefly depends for its water upon the store in the top six feet or so of soil, and that the moist soil below this yields up very little water by capillarity to the layers above. This is the contention of J. W. Leather,<sup>26</sup> who made a series of determinations of the amount of water at various times during the year in the uniform fine silt which constitutes the Indo-Gangetic alluvium at Pusa. From the fact that at about seven feet below the surface a layer occurred which contained the same proportion of water at the beginning and end of the dry period, Leather concludes that the loss of water by evaporation is confined to the higher levels, and that movements of water by surface tension from greater depths up to or near the surface do not take place. Leather's results, however, would be equally consistent with the view that the layer in question is in a condition not of static, but of dynamic, equilibrium as regards its water content, and that instead of losing no water to the layer above during the dry period, it has been balancing its losses by gains from below. The point can only be settled by determinations of the actual quantity of water lost by evaporation; considering the importance of this question of the rise of the subsoil water by surface tension or capillarity, it is very desirable that further experiments should be set on foot. So universally is the capillary uplift of water from the subsoil regarded as the source of the resistance of certain soils to drought, that it is surprising to find how few and untrustworthy are the data bearing on the subject.

The question of the flocculation of the finest soil particles by salts<sup>27</sup> has again been discussed by Rohland,<sup>28</sup> who connects it with the plasticity of the clay, the permeability of the soil to

<sup>26</sup> *Mem. Dept. Agric. India, Chem. Series*, 1908, 1, 79.

<sup>27</sup> *Ann. Report*, 1907, 269.

<sup>28</sup> *Landw. Jahrb.*, 1907, 36, 473; *A.*, ii, 59.

water, and its surface tension and absorptive power, all of which properties depend on the colloidal substances in the soil formed by the weathering of the felspars.

*Chemistry of the Growing Plant.*

The supposed photosynthesis, outside the plant, of formaldehyde and then of starch, by Priestley and Usher<sup>29</sup> has been subjected to severe criticism,<sup>30</sup> and their work is generally only regarded as affording support to the hypothesis that formaldehyde is the intermediate step between carbon dioxide and a sugar, although E. Baur<sup>31</sup> discusses the possibility of oxalic acid being the first stage in the synthesis.

The formaldehyde theory is supported by B. J. Harvey Gibson,<sup>32</sup> who has published a short note outlining a theory of photosynthesis, according to which the passage from carbon dioxide and water to formaldehyde is brought about by electric currents in the leaf tissue, generated by the incidence of the light rays. He is able to show by a new test that formaldehyde is present in all green leaves, the amount present bearing a definite relation to the illumination, and he also shows that a silent electrical discharge will generate formaldehyde in a solution of carbon dioxide. The electric currents in the leaf tissues and their variation with the illumination have been demonstrated by other investigators.

S. Strakosch<sup>33</sup> has been studying the other end of the assimilation process as it goes on in the leaf of the beet; he finds only dextrose in the mesophyll; sucrose appears later in the leaf veins after migration of dextrose has begun. Starch is not found until later still, after there has been some accumulation of sugars in the leaf. The formation of sucrose is dependent on light, but the amount of monosaccharides in the leaf remains almost constant whether the leaves are exposed to light or kept for some time in the dark. The sucrose migrates from the leaf to the root without undergoing any change, whereas, according to F. Strohmer,<sup>34</sup> when the reverse migration takes place in the second year of the plant's growth, the stored sucrose in the root is converted into invert sugar before it can be moved back to the leaf, where it is re-synthesised.

The old question of whether the endosperm of barley and similar

<sup>29</sup> *Proc. Roy. Soc.*, 1906, B, **77**, 369; *A.*, 1906, ii, 299.

<sup>30</sup> Ewart, *ibid.*, 1908, B, **80**, 30; *A.*, ii, 217; Mameli and Pollacci, *Atti R. Accad. Lincei*, 1908, [v], **17**, 1, 739; *A.*, ii, 881.

<sup>31</sup> *Zeitsch. physikal. Chem.*, 1908, **63**, 683; *A.*, ii, 790.

<sup>32</sup> *Ann. of Botany*, 1908, **22**, 117.

<sup>33</sup> *Zeitsch. Ver. deut. Zuckerind.*, 1907, 1057; *A.*, ii, 125.

<sup>34</sup> *Oesterr.-ung. Zeitsch. Zuckerind. Landw.*, **37**, 18; *A.*, ii, 726.

seeds possesses any vitality, or is to be regarded as a dead magazine of reserve food, has continued to attract attention. D. Bruschi<sup>35</sup> brings evidence to show that the vitality varies with the nature of the seed; all gradations may be observed between maize, in which the glutinous part of the grain is alive, and rye, in which the endosperm is wholly dead; wheat and barley being intermediate, in that a few layers of cells below the aleurone layer retain some vitality. F. Stoward<sup>36</sup> shows that the purely endospermic tissue of both barley and maize will respire and exchange carbon dioxide for oxygen, thus bringing evidence of another character in favour of the continued vitality of these cells.

The changes taking place in the nitrogenous compounds of plants when the proteins are hydrolysed during the germination of seeds and subsequently reformed in the growing shoot, continue to attract much attention, since on these very complex actions depend a good many technical differences of importance which the practical man sums up under the name of "quality" in the seeds or their products. H. T. Brown has published two important papers<sup>37</sup> on the soluble nitrogen compounds in malt and on the movements of such bodies from the endosperm into the embryo, as studied by presenting them to the detached embryo in water cultures. Asparagine was found to be the best nutrient, and was proved to exist in malt, but it was not settled whether it was to be regarded as a down- or an up-grade product. N. Wassilieff,<sup>38</sup> in studying the formation and migration of proteins during the ripening of seeds of lupins, finds asparagine in the unripe fruits, but regards it as an intermediate stage in the upbuilding of proteins from amino-acids, previously formed by the hydrolysis of proteins in the husks, etc. Scurti and Parrozzani<sup>39</sup> came to the conclusion that in the germination of sunflower seeds asparagine is not a down-grade product formed directly from the proteins, since it only is found during the more advanced stages of the germination process when the up-grade actions have begun.

The organic phosphorus compounds of seeds and plants are attracting increasing attention, and a number of papers<sup>40</sup> have

<sup>35</sup> *Ann. of Botany*, 1908, 22, 449.

<sup>36</sup> *Ibid.*, 415.

<sup>37</sup> *Trans. Guinness Lab.*, 1, ii, 288; *A.*, ii, 882; *J. Inst. Brewing*, 1907, 13, 394; *A.*, ii, 883.

<sup>38</sup> *Ber. Deut. bot. Ges.*, 1908, 26a, 454; *A.*, ii, 976.

<sup>39</sup> *Gazzetta*, 1908, 38, i, 216; *A.*, ii, 417.

<sup>40</sup> Stutzer, *Biochem. Zeitsch.*, 1907, 7, 471; *A.*, ii, 124; Suzuki and Yoshimura, *Bull. Coll. Agric. Tōkyō*, 1907, 7, 495; *A.*, ii, 124; Winterstein and Hiesstand *Zeitsch. physiol. Chem.*, 1908, 54, 288; *A.*, ii, 218; W. Windisch, *Jahrb. Vers. Lehr. Braueri.*, 1907, 10, 56; *A.*, ii, 528; E. Schulze, *Chem. Zeit.*, 1908, 32, 981; *A.*, ii, 977.

appeared on the determination of lecithin, phosphatides, phytin, etc., in plants. No general conclusions can yet be drawn, but these substances will have to be kept in mind in connexion with problems of ripening and quality.

In opposition to Willstätter,<sup>41</sup> Stoklasa, Brdlik, and Just<sup>42</sup> maintain that chlorophyll contains phosphorus, and is a lecithin-like substance which yields choline and glycerophosphoric acid among its decomposition products.

M. Wagner<sup>43</sup> describes a series of experiments to ascertain how variations in the nutrition, such as a deficiency or an excess of nitrogen, will affect the development of the plant in such characters as the relation of straw to corn, the time of ripening, etc. The experiments were made in pots with barley, oats, buckwheat, and mustard. It is not possible to draw any very general conclusions from the results, although the paper should not be neglected by anyone interested in the specific functions of the elements of nutrition; amongst other things, it is noticeable that the author's opinion is against the view that phosphoric acid gives a special stimulus to root development.

E. Molz<sup>44</sup> has published a long study of the well-known phenomena of chlorosis which occurs in the leaves of the vine and other plants, generally when growing on heavy calcareous soils. He associates its appearance with the formation of a putrefactive layer on the surface of the root, followed by the entry of calcium carbonate and the consequent neutralisation of the sap, and brings evidence to show that such conditions as would further any of these actions are recognised in practice as favourable to chlorosis. In one or two districts in England, fruit trees and allied plants are grown with difficulty because of their tendency to assume this chlorotic condition; the causes of the disease have never been cleared up, and it would be well if the cases were re-examined in the light of Molz's conclusions.

The stimulus to the growth of plants which has been ascribed to the salts of manganese forms the subject of several papers<sup>45</sup> published during the year, but the subject has received no real advancement, because it has not been settled if the supposed stimulus is due to direct action of the manganese on the plant or to some secondary

<sup>41</sup> *Annalen*, 1908, **358**, 267; *A.*, i, 199.

<sup>42</sup> *Ber. Deut. bot. Ges.*, 1908, **26a**, 69; *A.*, i, 279.

<sup>43</sup> *Landw. Versuchs.-Stat.*, 1908, **69**, 161; *A.*, ii, 1066.

<sup>44</sup> *Centr. Bakt. Par.*, 1907, ii, **20**, 71.

<sup>45</sup> H. von Feilitzen, *J. Landw.*, 1907, **55**, 289; *A.*, ii, 61; Uchiyama, *Doll. Imp. Centr. Agric. Exper. Stat. Japan*, 1907, **1**, 37; *A.*, ii, 126; W. F. Sutherst, *Transvaal Agric. J.*, 1908, **6**, 437; *A.*, ii, 528; Grégoire, Hendrick, and Carpioux, *Bull. Inst. Chim. Bact. Genbloux*, 1908, No. 75, 66; *A.*, ii, 529.

action on the soil. In all these stimulus effects the prime fact of the existence of increased growth also requires to be put beyond the reach of doubt, just as in the kindred case of the action of high tension electrical discharges on plants, an old question which has arisen again this year as the outcome of a large scale experiment near Worcester.<sup>46</sup>

### *Manures and Manuring.*

As regards fertilisers and manures, the record of the year is singularly blank. The new nitrogenous fertilisers, calcium cyanamide (either "kalk-stickstoff" containing free lime or "stickstoff-kalk" containing calcium chloride) and nitrate of lime, continue to be the subject of a number of field trials, because they are beginning to be put on the market in considerable quantities, but their behaviour is pretty much what was indicated in the earliest trials. Considerable dispute still rages as to the exact nature of the decomposition calcium cyanamide undergoes in the soil, and whether bacteria are essential in bringing about the change, as was originally maintained by Löhnis. A. D. Hall<sup>47</sup> has also published some experiments on the losses of ammonia experienced by cyanamide on storage under moist conditions, and on the practicability of mixing the fertiliser with superphosphate before sowing. The heat developed is not unmanageable, there are no losses of nitrogen, but the soluble phosphoric acid of the superphosphate becomes precipitated; the mixed fertiliser is, however, much more convenient for sowing than the original cyanamide.

M. Popp<sup>48</sup> has continued the well-known experiments of Wagner on the fertilising value of different compounds containing nitrogen, the experiments being made in pots, in some cases continued for three or four years. From the final summary, giving the mean of all the experiments, numbers like the following were obtained: If the returns from nitrogen in sodium nitrate be taken as 100, then an equivalent amount of nitrogen in dried blood will return 72, in horn meal 71, in castor cake 65, in bone meal 52. It has never been found possible to confirm these ratios in field work, where other factors come into play, particularly the influence of the fertiliser on the texture of the soil.

### *Chemistry of Animal Nutrition.*

Since it is generally accepted that during digestion the proteins of the food are very completely broken down to amino-acids, etc., before they are reconstructed in the intestinal wall, among the data

<sup>46</sup> *Nature*, 1908, **78**, 331.

<sup>47</sup> *J. Board Agric.*, 1908, **14**, 654.

<sup>48</sup> *Landw. Versuchs.-Stat.*, 1908, **68**, 253; *A.*, ii, 727.

required for an adequate theory of animal nutrition is a knowledge of the products of hydrolysis of all the proteins commonly occurring in feeding stuffs. Practical graziers know by experience that the proteins of all foods are not of equal value, nor is the same protein equally suited to all animals, but it is only recently that we see any means of placing these empirical results upon a scientific basis. Osborne and his co-workers have taken up this problem of the resolution of the vegetable proteins into their constituent amino-acids with great vigour, and during the year report <sup>49</sup> the results of the hydrolysis of amandin, gliadin, hordein, zein, vigin, legumin, legumelin, leucosin, and vicilin. A. Kleinschmitt <sup>50</sup> has also reported a hydrolysis of hordein. The imperfection of maize as a food is attributed by S. Baglioni <sup>51</sup> to the imperfect digestion of the zein, which yields on partial hydrolysis large quantities of phenylalanine in addition to phenolic compounds. The author sees some similarity between the symptoms of phenolic poisoning and those exhibited by animals dying through exclusive feeding on maize flour, but he does not seem to have taken into account the experiments of Miss Willcock and Hopkins, <sup>52</sup> who associate the nitrogen starvation which sets in when zein is the only nitrogenous food with the absence of tryptophan (and also lysin) from the zein molecule.

O. Kellner <sup>53</sup> discusses the lack of agreement between the amount of digestible protein in a feeding stuff as determined by pepsin, etc., and the figures, varying in themselves, obtained from estimations of the nitrogen in the faeces of different animals. For example, the digestion coefficient of the crude protein of potatoes, as determined by feeding experiments, was 31.9 with sheep and 53.8 with pigs. Kellner considers that these differences are only partly due to the intestinal slime, etc., containing previously digested nitrogen, but are in the main caused by the bacteria in the intestine which build up insoluble proteins in the faeces from protein matter that has previously been digested, or from non-protein nitrogen compounds in the food. The many other papers which have been published on nutrition and digestion questions are mainly of technical interest and do not break new ground.

<sup>49</sup> *Amer. J. Physiol.*, 1908, **20**, 470, 477, 493; *A.*, i, 115; *Amer. J. Physiol.*, 1908, **22**, 362, 423; *A.*, i, 744, 843; *J. Biol. Chem.*, 1908, **5**, 187; *A.*, i, 928, 929.

<sup>50</sup> *Zeitsch. physiol. Chem.*, 1907, **54**, 110; *A.*, i, 69.

<sup>51</sup> *Atti R. Accad. Lincei*, 1908, [v], **17**, i, 609; *A.*, ii, 619.

<sup>52</sup> *Ann. Report*, 1907, 276.

<sup>53</sup> *Landw. Versuchs.-Stat.*, 1908, **68**, 463.

*Analytical.*

Attention may be directed to two papers on the determination of small quantities of nitrogen and carbon in soils by Chouchak and Pouget,<sup>54</sup> which may occasionally prove useful when only a small amount of material is available, although it is difficult to see what superiority the method for nitrogen possesses over the Kjeldahl process followed by an estimation of the ammonia in the distillate by nesslerising, nor does the method for carbon promise to be more accurate than the modified wet combustion process.<sup>55</sup>

A. D. HALL.

<sup>54</sup> *Bull. Soc. chim.*, 1908, [iv], 1, 1173, 3, 75 ; *A.*, ii, 223, 225.

<sup>55</sup> *Trans.*, 1906, 89, 595.



## CRYSTALLOGRAPHY.

THE modes in which the behaviour and properties of crystalline substances can influence chemical theory may be roughly classified under two headings. First, including those in which, with our present knowledge, no special interest attaches to the crystalline nature of the solid substance; into this category fall all questions of the solubility of crystalline substances, and of the equilibrium between liquid and crystalline phases, or between two crystalline phases. Questions of this kind are not discussed in the present Report, because their experimental treatment has not yet progressed so far as to render of importance the differences in surface character presented by the various kinds of crystal faces occurring on one substance, and also because they properly form part of the report on physical chemistry. The second category embraces the relation between the crystal structure and the chemical nature of substances, and to this subject alone the present Report is confined.

As a result of the study of crystalline structure, both in its experimental and theoretical aspects, during the past hundred years, it may be stated that the whole of the physical, geometrical, and mechanical properties of crystalline substances are in harmony with the following geometrical definition. A crystalline structure is a homogeneous one, that is, a structure the parts of which are uniformly repeated throughout, corresponding points having everywhere a similar environment. The correspondence between this statement and the facts is so complete as to prove definitely that the characteristic which distinguishes crystals from all other bodies is this homogeneity of structure. From the principle of structural homogeneity may be at once deduced the various forms in which the empirically observed fundamental law of crystallography has been stated, such as the law of zones, the law of rational indices, etc., and it is to be concluded that the distinguishing feature of external regularity of form assumed by a crystalline substance is correlated with the class of homogeneous structure to which it belongs.

An investigation into the structure of crystalline substances, as

defined above, may be regarded as involving two distinct inquiries. The first of these is concerned with the kinds of homogeneous structure geometrically possible, and the second, with the nature of the units of which the homogeneous structure is built up. The first inquiry, regarded as a purely geometrical one, has now been prosecuted to a stage approaching finality. The second inquiry involves the application of geometrical methods to specific cases which have been experimentally investigated; its pursuit is attended with much difficulty, and it is but in the early stages of development.

The work which has been done on the possible kinds of homogeneity of structure has been well summarised in a report to the British Association on the structure of crystals,<sup>1</sup> so that it will suffice now to indicate very briefly and roughly the successive stages by which our present highly complete knowledge of the subject has been attained. These stages are three in number.

(1) Bravais (1850) effected an exhaustive inquiry into the various ways in which small identical regular bodies can be distributed uniformly throughout unlimited space, so that every one of them has the remainder of the assemblage arranged about it in an identical manner, and with the same orientation. The last condition involves the property that a linear translation of the entire assemblage, the length and direction of which are those of a line joining the centres of any two of the bodies, produces coincidence of the moved assemblage with the assemblage as it stood before the translation; the centres of the bodies consequently form a parallelepipedal network or a so-called "space-lattice." Bravais showed that fourteen kinds of such space-lattices exist, and that these correspond in their symmetry with the seven large crystal systems. It may be noted that any movement or operation, such as the translation just mentioned, which, after performance, leaves the assemblage identical in aspect with its original, is conveniently termed a "coincidence movement"; in addition to the linear translations, some of the Bravais space-lattices possess other coincidence movements which are rotations about axes. The occurrence of rotations about an axis as coincidence movements is expressed by naming that axis one of symmetry, and, if the angular rotation producing coincidence is  $360^\circ/n$ , the axis is described as one of  $n$ -fold symmetry. The axial ratios of a crystalline substance, stated in the customary form of the value of  $a:b:c$ , represent the ratio of three linear translations of the space-lattice distributed in three-dimensional space.

(2) Sohncke (1876) determined the possible kinds of homogeneous

<sup>1</sup> *Brit. Assoc. Report*, Glasgow, 1901, 297.

arrangement derivable by enlarging Bravais's definition, the modification consisting in the abandonment of the condition that the similar environments of the units must be similarly orientated. This change of definition abolishes the necessity for attributing any axial crystal symmetry to the unit itself, and renders possible the geometrical dissection of every symmetrical Bravais unit into identical smaller units devoid of axial symmetry. Substituting mere points or small spheres for Bravais's small regular bodies, and making the former as numerous as the coincidence movements, axial and translational, of the system under consideration, Sohncke makes the configuration, namely, the coincidence movements of his systems of points, express all the identical repetition of parts present. He discriminates sixty-five types of homogeneous structure, and these are known as Sohncke systems; in addition to the kinds of crystal symmetry exhibited by the Bravais space-lattices, the Sohncke systems furnish types corresponding in symmetry with most of the thirty-two crystal classes into which the seven large crystal systems are subdivided.

(3) The final step soon followed Sohncke's important development of the possible ways of deducing homogeneous structures. It was perceived that the coincidence movements of a Sohncke system represent only identical repetition of parts, and leave enantiomorphous likeness (or mirror-image resemblance) of parts to be expressed by some added condition. Bravais had modified the symmetry of some of his space-lattices to meet this requirement by attributing to his small bodies the lower symmetry needed for correspondence with the facts. To avoid the necessity for any such unsatisfactory contrivance, a further modification of the condition of similar environment was now resorted to; it was seen that two points in an assemblage are similarly, although not identically, environed if the arrangement of the unlimited assemblage about one of them is the mirror-image of its arrangement about the other; also that coincidence operations about centres of symmetry or planes of symmetry then perform the function fulfilled in the Sohncke systems by the coincidence movements, and express the relation between similar points enantiomorphously related. Fedoroff, Schönflies, and Barlow independently investigated the additional forms supplied by this enlarged conception of similarity of environment, and proved that the admission of coincidence operations connecting similar points, the environments of which present mirror-image similarity, leads to the discrimination of many more types of symmetry; the latter now provide representatives of all the thirty-two classes of crystal symmetry. The investigators just named are agreed that the total number of types of symmetrical

structure made possible by the further enlargement of definition defined above is 230, and these are described as the 230 types of point-systems. As no kind of operation, other than such as are employed in the Sohncke systems and the systems derived from them by mirror-image duplication, can form a component of a coincidence operation consistent with homogeneity of structure, the first part of the inquiry into crystal structure, that dealing with the mode of arrangement of the parts, is virtually ended.

A simple illustration will make clear the distinction between the three kinds of similarity of position of members of a flock of similar parts just described. Consider a stack of cubes, such as are used by children, built up in the ordinary way, so that the cubes are in face contact, and so that throughout the stack each cube corner makes contact with seven other cube corners. The assemblage of points formed by the cube corners is a Bravais space-lattice.

Each point in this space-lattice is common to twelve cube faces, each cube face being also common to two cubes in contact. Replace one point of the space-lattice by a cluster of twelve points, one lying on each diagonal of a cube face drawn from the original point, and all being equidistant from the original point. Repeat this process throughout the system until each point of the space-lattice is similarly and symmetrically replaced by a cluster of twelve. The assemblage built up by this symmetrical repetition throughout space of the cluster of twelve points about the original cube corners of the space-lattice is a Sohncke system, and consists of twelve interlaced space-lattices which are related by simple axial rotations: all the points are identically related to the entire unlimited assemblage.

Next displace each point in a cluster of twelve from the plane of the cube face in which it lies, all the twelve being moved similarly, symmetrically, and in the corresponding direction, to points just within the cubes; this operation can be so performed that the resulting twelve-point cluster is no longer identical with its mirror-image. Treat an adjacent cluster in the same way, but making the arrangement identical with the mirror-image of the first, and repeat these operations symmetrically and alternately throughout space until all the original twelve-point clusters have been appropriately displaced; one of the 230 point systems is thus generated. It consists of a Bravais space-lattice in which each point is replaced by a twelve-point cluster of enantiomorphous form disposed about the original point; one-half of the clusters have the right-handed, the others the left-handed, configuration. The assemblage may be also regarded as an interpenetration of a right- and a left-handed Sohncke system, one, namely, which is

derived by a mirror-image repetition of either the right- or the left-handed component Sohncke system.

After this necessarily brief and incomplete sketch of the results arrived at in the inquiry as to the mode of arrangement of parts holding in crystalline structures, attention may be directed towards the second kind of problem involved, that, namely, of the nature of the parts which are arranged. During the past century exact data concerning the crystalline forms of some thousands of substances have been obtained, and these are now being collected and republished by Paul Groth.<sup>2</sup> Although until very recently no comprehensive scheme had been advanced for reconciling the crystalline form and chemical nature of substances in general, several results obtained, and conclusions drawn, stand out beyond others as indications for the construction of such a scheme. The fact that certain definite laws are revealed in the enormous number of observations made of crystalline forms has led to the conviction that the geometrical and physical properties of a crystalline material are absolutely characteristic, and are, consequently, functions of the chemical composition, constitution, and configuration of the substance: the discovery by Mitscherlich (1819) of the general facts of isomorphism, and that substances of the same chemical type exhibit almost identical crystalline forms, has greatly strengthened, not, as was originally anticipated, weakened, this conviction. Pasteur's law, that substances of enantiomorphous molecular configuration affect enantiomorphous crystalline structures, and that the crystal structures assumed by enantiomorphously related molecular configurations are themselves enantiomorphously related, has been the subject of considerable controversy.<sup>3</sup> The law may now be regarded as vindicated, and possesses importance in connexion with the interdependence of crystalline form and chemical constitution.<sup>4</sup> Groth placed the subject of morphotropy on a sound basis by pointing out that derivatives of benzene, which are not so closely related as to be isomorphous, frequently exhibit marked quantitative resemblances in crystalline form; this, again, indicated the existence of a function connecting crystalline form and chemical constitution. All these discoveries now form parts of the history of chemical crystallography, and have proved the basis of important developments. No less importance attaches to several more recent extensions of our knowledge, which may now be briefly discussed.

<sup>2</sup> *Chemische Krystallographie*, Leipzig, 1806, *et seq.*

<sup>3</sup> Walden, *Ber.*, 1896, **29**, 1692; *A.*, 1896, ii, 553; Kipping and Pope, *Trans.*, 1897, **71**, 989; Barlow, *Phil. Mag.*, 1897, [v], **43**, 110.

<sup>4</sup> Pope and Harvey, *Trans.*, 1901, **79**, 828.

Tschermak has pointed out<sup>5</sup> the frequent occurrence of a striking relation between the numerical proportions in which atoms of different elements are present in the molecule of a substance and the nature of the symmetry presented by the crystalline form. He notes that compounds in the molecular formulæ of which the numbers 2 and 3 or 6 occur as denoting the numbers of atoms of various elements present, tend to crystallise in the rhombohedral or the hexagonal system; these crystalline systems are characterised by the possession of axes of two- and three- or six-fold symmetry. As instances may be quoted the compounds of the following compositions:  $\text{Fe}_2\text{O}_3$ ,  $\text{FeCl}_3$ ,  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ag}_3\text{SbS}_3$ ,  $(\text{C}_6\text{H}_5)_3\text{C} \cdot \text{OH}$ ,  $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{PI}_3$ , and  $\text{CHI}_3$ . Similarly, those substances in the molecular formulæ of which the number 4 occurs, but not the number 3, in a large proportion of cases crystallise in the tetragonal system; this system possesses axes of two-fold and four-fold symmetry, but not of three-fold symmetry. As typical examples, the following substances may be noted:  $\text{ZrSiO}_4$ ,  $\text{GfSO}_4 \cdot 4\text{H}_2\text{O}$ ,  $(\text{C}_6\text{H}_5)_4\text{Si}$ , and  $\text{C}(\text{CH}_2 \cdot \text{OH})_4$ . In the same way, compounds in the molecular compositions of which the numbers 4 and 3 occur tend to crystallise in the cubic system, this system possessing axes both of three- and of four-fold symmetry; as illustrations the compositions of the following cubic substances may be quoted:  $3\text{KF} \cdot \text{ZrF}_4$ ,  $\text{Ag}_3\text{PO}_4$ ,  $\text{As}_4\text{O}_6$ , and  $\text{K}_2\text{SO}_4 \cdot \text{Al}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ . Tschermak's conclusions are of great significance as condemnatory of the view still occasionally advanced that the individuality of the atom is entirely lost when it enters into molecular combination.

The axial ratios by means of which the crystalline form of a crystalline substance are described are the ratios of some of the translations occurring in the homogeneous structure of the crystal. In passing from a given substance to one isomorphous with it, the axial ratios in general change to a greater or less extent; but inasmuch as each set of axial ratios consists merely of ratios of the actual dimensions of the corresponding homogeneous structure, the comparison of the axial ratios of two isomorphous substances does not reveal the change in dimensions which has accompanied the passage from one substance to the other. The three translations, the ratios alone of which are given by the axial ratios  $a : b : c$ , in general all change during such a transition. More information can, however, be obtained by the consideration of a solid figure of which the volume is the molecular volume,  $M$ , of the substance, and the linear dimensions,  $\chi$ ,  $\psi$ , and  $\omega$ , are in the ratio,  $a : b : c$ , of the axial ratios; the linear dimensions of the solid figure, measured in the three axial directions, indicate for a series of

<sup>5</sup> *Tsch., Min. Mitt.*, 1903, 22, 393.

isomorphous substances the absolute changes in magnitude of corresponding translations of the homogeneous structure common to the substances which occur in passing from one member of the series to another. In either of the rectangular systems the values of  $\chi$ ,  $\psi$ , and  $\omega$ , which are termed the 'topic parameters' or the 'molecular distance ratios,' are the following:

$$\chi = \sqrt[3]{\frac{a^2 M}{c}}, \quad \psi = \sqrt[3]{\frac{M}{ac}}, \quad \omega = \sqrt[3]{\frac{c^2 M}{a}}.$$

Further,  $\chi\psi\omega = M$ , and  $a:b:c = \chi:\psi:\omega$ . The molecular distance ratios were introduced by F. Becke,<sup>6</sup> and measure the absolute changes in dimensions which a definite parallelipedal molecular unit of the structure undergoes during the passage from one crystalline substance to another or others isomorphous with it. They were applied by W. Muthmann<sup>7</sup> to the investigation of the alkali permanganates, and from the differences between corresponding molecular distance ratios observed amongst the various salts of the series, the conclusion was drawn that the unit of the crystalline structure is composed of four chemical molecules. The extension of this work to the alkali perchlorates, which are isomorphous with the permanganates, has furnished T. V. Barker<sup>8</sup> with results which are not in agreement with Muthmann's conclusion. The way in which the axial ratios and the molecular distance ratios are related is shown in the following table, which gives the values for the alkali permanganates:

	$a$	$b$	$c$	$M$	$\chi$	$\psi$	$\omega$
KMnO <sub>4</sub> .....	0.7972	1	0.6491	58.526	3.8554	4.8360	3.1390
RbMnO <sub>4</sub> .....	0.8311	1	0.6662	63.228	4.0322	4.8517	3.2312
CsMnO <sub>4</sub> .....	0.8683	1	0.6853	70.042	4.2555	4.9009	3.3584
NH <sub>4</sub> MnO <sub>4</sub> ...	0.8164	1	0.6584	62.126	3.9767	4.8711	3.2071

It will be seen that whilst the axial ratios only measure the relative dimensions of translations in the homogeneous structure in the case of any one substance, because one axial dimension, that of the axis  $b$ , is taken as unity, the molecular distance ratios indicate, in addition, the relative dimensions of corresponding translations in the several members of an isomorphous series.

The molecular distance ratios have been very systematically applied by A. E. H. Tutton to the investigation of a long series of salts,<sup>9</sup> and the kind of information which they are capable of yielding is well illustrated by this author's numbers for the alkali sulphates and selenates.

<sup>6</sup> *Sitzungsber. K. Akad. Wiss. Wien*, 1893, **30**, 204.

<sup>7</sup> *Zeitsch. Kryst. Min.*, 1894, **22**, 497; *A.*, 1894, ii, 181.

<sup>8</sup> *Ibid.*, 1907, **43**, 529.

<sup>9</sup> *Trans.*, 1894, **65**, 688; 1905, **87**, 1183.

	$\chi$	$\psi$	$\omega$
$K_2SO_4$ .....	3.8810	3.8574	4.9964
$Rb_2SO_4$ ....	4.0340	4.0039	5.2366
$Cs_2SO_4$ .....	4.2187	4.1849	5.2366
$K_2SeO_4$ .....	4.0291	4.0068	5.1171
$Rb_2SeO_4$ ....	4.1672	4.1315	5.3461
$Cs_2SeO_4$ .....	4.3457	4.3040	5.6058

The comparison of these figures shows that in passing from the sulphate or the selenate of one alkali metal to that of its neighbour in the periodic classification, the greatest change in the molecular distance ratios is in  $\omega$ , which is measured in the vertical direction of the axis  $c$ ; the horizontally measured dimensions  $\chi$  and  $\psi$  experience much less change. In passing from a sulphate to the corresponding selenate, variation in the opposite sense is observed; the values of  $\chi$  and  $\psi$  change more than does that of  $\omega$ . From these results Tutton concludes that the molecules of the alkali sulphates and selenates are so disposed in the crystal structure that one atom of sulphur or selenium lies between two of the alkali metal, and that all three are extended in the direction of the vertical axis  $c$  or of  $\omega$ . He claims that the further analysis of his results enables him to identify the particular point system of the 230 which characterises the crystal structure of these salts.

In order that the notion of molecular distance ratios may be successfully applied to series of isomorphous substances, it is essential that the axial ratios used in their calculation should be the ratios of corresponding translations in the crystal structures of a type common to the several members of the series; the known condition that the axial ratios of isomorphous substances approximate closely to each other, in general renders it easy to ensure this. The molecular distance ratios have, however, also been extensively applied to morphotropically related substances, and here it is frequently difficult to ensure that the axial ratios, and even the axial directions, selected for the calculation, refer to corresponding directions and dimensions in the homogeneous structures of the several members of the morphotropic series. The series of values stated in the following table are given by F. Slavík.<sup>10</sup>

Crystal system.	$NH_4I$ . Cubic.	$NMe_4I$ . Tetragonal.	$NEt_4I$ . Tetragonal.	$NPr_4I$ . Orthorhombic.
$M$ .....	57.51	108.70	162.91	235.95
$\chi$ .....	3.860	5.319	6.648	6.093
$\psi$ .....	3.860	5.319	6.648	7.851
$\omega$ .....	3.860	3.842	3.686	4.933

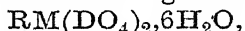
These numbers suggest that on replacing the four hydrogen atoms in ammonium iodide by four methyl or four ethyl groups, the main

<sup>10</sup> *Zeitsch. Kryst. Min.*, 1902, **36**, 268; *A.*, 1902, ii, 561.



change in dimensions of the crystal structure occurs in the directions of the axes  $a$  and  $b$ , in which the dimensions  $\chi$  and  $\psi$  are measured; it is not, however, immediately evident that the values of the axial ratios,  $a : b : c$ , have been so chosen in the case of tetrapropylammonium iodide as to correspond with those used in the case of the other members of the series. Another interesting series of alkyl derivatives, those of carbamide, has been worked out by G. Mez.<sup>11</sup> In connexion with this question, it may be remarked that the practice, now very general, of publishing the molecular distance ratios of isolated substances is useless, as the values only possess significance when compared with appropriately selected molecular distance ratios of related compounds.

During the past twenty years Tutton has carried out a remarkable series of crystallographic measurements, the results of which are, for the most part, published in the Transactions of the Chemical Society. He has studied, in the majority of cases with the aid of specially designed measuring instruments, the orthorhombic sulphates and selenates of potassium, rubidium, caesium, ammonium, and thallium, and many members of the series of monosymmetric double salts of the general composition



in which R is K, Rb, Cs, or  $\text{NH}_4$ , M is Mg, Zn, Fe, Ni, Co, Mn, Cu, or Cd, and D is S or Se. In addition to the determination of the crystalline form and the refraction constants, the coefficients of expansion by heat, and other properties of these materials have been ascertained in the different principal directions of the crystal structure. Amongst the principal conclusions which Tutton has drawn are that in each case the crystalline form and other properties of the rubidium salt are intermediate between those of the corresponding potassium and caesium salts, and that, in the case of the double salts, the alkali metal exerts a predominant influence in determining the crystalline form; it is also shown that the effect of introducing the ammonium radicle in place of a potassium atom is nearly the same as that of similarly substituting a rubidium for a potassium atom. Tutton summarises his conclusions in a general law which states that,<sup>12</sup> in an isomorphous series in the strictest sense, where the interchangeable elements belong to the same family group of the periodic classification, the whole of the properties of the crystals, morphological, optical, thermal, and physical, in general are functions of the atomic weights of these elements; the sulphates and selenates of potassium, rubidium, and caesium, of which the molecular distance ratios are quoted on p. 265,

<sup>11</sup> *Zeitsch. Kryst. Min.*, 1902, **35**, 242; *A.*, 1902, i, 86.

<sup>12</sup> *Proc. Roy. Soc.*, 1907, **79** A 381; *A.*, 1907, ii, 688.

belong to such a series, which, for the purpose of distinguishing the closeness of the relations connecting its several members, is termed a "eutropic series." Thallium sulphate and selenate and ammonium sulphate are only isomorphous with the previously mentioned eutropically related salts in a less rigid sense; this may be expressed by saying that thallium and ammonium are capable of changing places with potassium, rubidium, and caesium without altering the crystal system and without causing angular and structural changes of much greater magnitude than those produced by the interchange of members of the same family group of elements. An isomorphous series, in this wider sense, is defined as one the members of which bear some definite chemical analogy and crystallise according to the same system and in the same class of that system, and develop the same forms inclined at angles which only differ by a few degrees, rarely exceeding  $3^{\circ}$ . A eutropic series is one in which these small angular differences, and also the structural and physical properties of the crystals, obey the law of progression according to the atomic weights of the interchangeable elements which give rise to the series and which belong to the same family group. Thus thallium sulphate and selenate and ammonium sulphate belong to the isomorphous orthorhombic series,  $R_2(S,Se)O_4$ , whilst the sulphates and selenates of potassium, rubidium, and caesium belong, not only to this isomorphous series, but also to the more exclusive eutropic series included within it. The intimate relationship thus exhibited between potassium, rubidium, and caesium is of similar nature to that expressed by associating these three metals together as one Döbereiner triad in the periodic classification. Two general propositions, which could not previously be substantiated, are established by Tutton's work. First, that goniometric measurements can be made on carefully prepared materials of high purity, which possess a degree of accuracy comparable with that of atomic weight determinations. Secondly, proof is repeatedly found that the substitution of one particular element by another produces a quantitatively similar change in dimensions of the crystal structure, in whatever salt the substitution is made; this result constitutes a great advance, because it shows that each atom entering into a crystalline structure produces a definite and constant crystallographic effect, and indeed indicates the mode in which attempts should be made to define that effect as a constant of the element concerned.

The need for some distinction, such as that drawn by Tutton between a eutropic and an isomorphous series, has also been recognised by T. V. Barker,<sup>13</sup> who has investigated the mode in which

<sup>13</sup> *Trans.*, 1906, **89**, 1143; *Mén. Mag.*, 1907, **14**, 235; 1908, **15**, 42; *A.*, 1907, ii, 240; 1908, ii, 366.

substances crystallise from solution upon surfaces consisting of crystalline plates of other materials. The crystals which separate from the solution are in many cases found to assume a definite orientation with respect to principal crystallographic directions in the crystalline surface upon which they form; the one substance is then said to form parallel growths upon the other. Examination of this property, that of forming solid solutions, and a number of others, as exhibited by the cubic cyanides and halogen salts of ammonium and the alkali metals has led Barker to classify these compounds in two "isostructural" groups, the members within either of which are especially closely related to each other. It is concluded that no direct connexion exists between the formation of parallel growths and of solid solutions, although the two properties are favoured by the same factor, namely, similarity of molecular volume.

Attention may now be directed to a mode of treating the second kind of crystallo-chemical problem distinguished earlier in the Report, which offers a systematic scheme for the quantitative correlation of crystallographic facts of chemical importance, and defines the relation subsisting between crystalline form and chemical composition, constitution, and configuration. W. Barlow and W. J. Pope<sup>14</sup> have adopted, for motives of convenience, a method of regarding the whole of the volume occupied by a crystalline structure as partitioned out into polyhedra, which lie packed together in such a manner as to fill the whole of that volume without interstices. The polyhedra can be so selected that each represents the habitat of one component atom of the material, and are termed the spheres of atomic influence of the constituent atoms. Up to this point no assumption is made other than that clearly indicated by the results of crystallographic measurements, namely, that each atom present in a crystalline structure exerts a distinct morphological effect—or, what is the same thing, appropriates a certain definite volume. The assumption is next made that the crystalline structure, which is resolvable into individual molecules and ultimately into individual atoms, exists as such by reason of equilibrium set up between opposing attractive and repulsive forces operative between the component atoms, and that this equilibrium results in the polyhedra representing the spheres of atomic influence assuming shapes which are as nearly as possible spherical. The application of the new method of treatment and the assumption defined are shown to bring immediately into quantitative correspondence a great variety of crystallographic data which could not

<sup>14</sup> *Trans.*, 1906, **89**, 1675; 1907, **91**, 1150; 1908, **93**, 1528.

previously be interpreted, and to lead to noteworthy conclusions respecting valency and chemical constitution, which can be, and have since been in part, verified by purely chemical methods.

In harmony with the assumption that the spheres of predominant atomic influence tend towards sphericity, the polyhedra thus arrived at may be regarded as derived by compression of a close-packed assemblage of deformable incompressible elastic spheres, the compression sufficing for the practical extinction of the interstitial space. When such an assemblage is released from pressure it is evident that in place of polyhedra, the shapes of which approximate as closely as possible to the spherical, closely-packed spheres are presented; the distances between the sphere centres can be substantially in the same ratios as the distances between the centres of the corresponding polyhedra in the unexpanded mass, and the equilibrium condition of maximum sphericity of the polyhedra will be represented in the expanded mass of spheres by the existence of the maximum number of contacts between spheres. The whole method of treating the primary assumption thus resolves itself into finding close-packed assemblages of spheres of various sizes representing by their relative volumes the spheres of influence of the component atoms of any particular crystalline structure.

For illustrative purposes, the comparatively simple case presented by the crystalline elements may be presented. If the atoms of an element are all similar, and if their grouping into molecular complexes does not appreciably affect the relationship existing between neighbouring atoms, the crystalline form assumed by the element should have the symmetry and dimensions of the closest-packed assemblage of equal spheres. There are, however, two such closest-packed assemblages,<sup>15</sup> one of cubic symmetry, in which the symmetry defines all the dimensions, and the other of hexagonal symmetry, in which the ratio of a horizontal translation,  $a$ , to a vertical translation,  $c$ , is  $a:c=1:1.6330$  or  $1:1.4142$ . Of the crystalline elements, 50 per cent. are cubic and 35 per cent. are hexagonal, and, so far as data have been collected, the axial ratios of the hexagonal elements approximate to the values of  $a:c$  quoted above.

Suppose, however, that some complicating factor is operative in determining the crystalline form of the element, such, for instance, as a molecular aggregation holding certain sets of atoms together in positions of some restraint; this should disturb the simplicity of the relation indicated above, and should result in the crystalline form departing to a greater or lesser extent from the closest-packed

<sup>15</sup> *Trans.*, 1907, 91, 1159.

cubic or hexagonal arrangement of equal spheres. Those elements which are neither cubic nor hexagonal would therefore be expected to assume crystalline forms approximating closely to the cubic or hexagonal arrangement indicated. An inspection of the geometrical data for the few elements which are neither cubic nor hexagonal shows that they are all so closely allied to the forms indicated that a very slight distortion would make them wholly cubic or hexagonal. It is further very significant that those elements which exhibit characteristics usually associated with particular types of molecular aggregation, such as colour, existence in allotropic modifications, etc., are the ones which differ most markedly in crystalline form from the simple cubic and hexagonal structures indicated; thus, whilst ordinary phosphorus and diamond are cubic, red phosphorus and graphite are respectively orthorhombic and monosymmetric. Consideration of the crystalline structure and the twinning of diamond, together with its relations to graphite, have led W. J. Sollas<sup>16</sup> to suggest the cubic closest-packed arrangement of equal spheres as representing the crystal structure of diamond, and the tetrahedrally arranged groups of four spheres, into which that arrangement is homogeneously partitionable, as representing the molecules of this allotropic form of carbon.<sup>17</sup>

On turning to the binary compounds, such as NaCl, KI, AgI, and ZnO, a further advance is indicated. The molecules of nearly all binary compounds consist of two atoms of undoubtedly equal valency, and of these 68·5 per cent. are cubic and 19·5 per cent. hexagonal, the axial ratios of the latter in every case approximating very closely to the theoretical value of  $a:c=1:1\cdot6330$ , indicated above. Whilst, however, the crystal forms of the cubic and hexagonal elements nearly all belong, so far as is known, to the holohedral crystal classes, those of the binary compounds belong to the less symmetrical hemihedral, tetartohedral, or hemimorphous classes of the two systems. By allocating, in the cubic or hexagonal closest-packed assemblage above referred to, one-half of the polyhedral cells, appropriately selected, to the one kind of component atoms, and the remainder to the other element present in the compound, the cubic or hexagonal crystalline form, with its appropriate corresponding hemi- or tetarto-hedrism or hemimorphism, can be precisely imitated. Other peculiarities of the crystalline structure, such as the existence of gliding planes in the alkali halogen compounds and the interconversion of the cubic and hexagonal modifications of silver iodide, can also be exactly simulated. Each of the assemblages

<sup>16</sup> *Proc. Roy. Soc.*, 1901, **67**, 493.

<sup>17</sup> Compare also *Sci. Proc. Roy. Dubl. Soc.*, 1897, **8**, 542, and *Trans.*, 1906, **89**, 1741.

thus devised can be geometrically partitioned into similar units composed of two adjoining spheres of atomic influence, one of each element; these, it may be premised, represent the molecules of the binary compound as they occur in the crystal structure.

The close imitation of the crystalline behaviour of the binary compounds by the closest-packed assemblages of polyhedra or spheres, briefly described above, points to a conclusion of a novel kind, the correctness of which has been repeatedly confirmed in the course of the work now under review. The conclusion is that the volumes appropriated by the polyhedra representing the spheres of atomic influence in any crystalline structure are approximately proportional to the numbers representing the valencies of the respective elements concerned. Further investigation seems to show that in every case hitherto studied the valency thus exhibited by an element is the lowest which its chemical behaviour assigns to it; this valency is conveniently distinguished as the fundamental valency of the element. The crystalline forms of the substances  $\text{CsI}_3$ ,  $\text{TlI}_3$ , and  $\text{CsI}_3$ , for example, are all in accordance with the view that the constituent elements are fundamentally univalent. The law thus enunciated is termed the law of valency volumes.

It is not indicated that the volumes of the spheres of atomic influence are rigidly proportional to the whole numbers representing the fundamental valencies; on the contrary, the volumes only approximate to the whole number ratios, and an analysis of the data for the crystalline trihalides of the alkali metals shows that throughout the measured series of sixteen salts, the volume of the sphere of atomic influence increases slightly in passing from potassium to rubidium to caesium, and from chlorine to bromine to iodine. The sphere of atomic influence of thallium in thallic iodide is almost identical in volume with that of rubidium in rubidium triiodide. The indication thus obtained of the invariability of magnitude of the sphere of atomic influence of any particular element is in complete agreement with the general result drawn from Tutton's work, namely, that the dimensional influence exercised on the crystal structure by a particular atom is constant. The close approximation to identity between the volumes of the spheres of atomic influence of rubidium and thallium in the salts  $\text{TlI}_3$  and  $\text{RbI}_3$  is striking in view of Tutton's demonstration that rubidium and thallic sulphates have almost the same crystallographic dimensions.<sup>18</sup>

The law of valency volumes noted above indicates that a very close relationship exists between the crystalline form of a substance and the fundamental valencies of the component elements. It should

<sup>18</sup> *Proc. Roy. Soc.*, 1907, **79**, A, 351; *A.*, 1907, ii, 688.

consequently be possible to elucidate by its aid all those morphotropic similarities between the crystal forms of substances of allied constitutions which in the past have been at once so striking and so mysterious; this can, indeed, be done by substituting, in the calculation of the molecular distance ratios, the molecular volume by the sum of the valencies of the atoms constituting the molecule. By this means a method is obtained of comparing the dimensions of translations in the crystalline structures of a series of morphotropically related substances, on the assumption that, under such conditions, each atom throughout the series reserves for its own occupation a volume proportional to the number representing its fundamental valency. The sum of the valencies of the atoms composing the molecule, the so-called "valency volume," being  $W$ , the required translation ratios, or the "equivalence parameters,"  $x$ ,  $y$ , and  $z$ , are given in the rectangular crystalline systems by:

$$x = \sqrt[3]{\frac{a^3 M}{c}}, \quad y = \sqrt[3]{\frac{M}{ac}}, \quad z = \sqrt[3]{\frac{c^3 M}{a}}.$$

The further relations hold that  $xyz = W$  and  $x:y:z = a:b:c$ .

If morphotropic relationships are correlated by means of the equivalence parameters, it is evident that strong confirmation of the truth of the law of valency volumes is obtained. The study of a number of cases shows this prediction to be amply verified,<sup>19</sup> and the following may be quoted in order to show the nature of the relation established.

*d*-Camphoric anhydride,  $C_{10}H_{14}O_3$ , and the additive compound of *d*-camphoric acid with acetone,  $C_{10}H_{16}O_4, \frac{1}{2}(CH_3)_2CO$ , are both orthorhombic, and are closely related through their axial ratios; the latter values and those of the corresponding equivalence parameters are stated below:

	$W$ .	$a : b : c$ .	$x : y : z$ .
$\alpha$ - $C_{10}H_{14}O_3$ .....	60	1.0011 : 1 : 1.7270	3.265 : 3.262 : 5.633
$\alpha$ - $C_{10}H_{16}O_4, \frac{1}{2}Me_2CO$ ...	74	1.2386 : 1 : 1.7172	4.043 : 3.265 : 5.606

The axial ratios show that the whole of the morphological effect of introducing the elements of  $H_2O, \frac{1}{2}Me_2CO$  into the molecule of camphoric anhydride is exerted in the direction of the axis  $a$ ; the equivalence parameters show that the magnitude of this effect is proportional to the sum of the valencies of the increment thus introduced. Other instances of the kind are found amongst the humite minerals,<sup>20</sup> and the substances related to "saccharin." F. M. Jaeger has also demonstrated<sup>21</sup> that predictions concerning the

<sup>19</sup> *Trans.*, 1906, **89**, 1680.

<sup>20</sup> *Ibid.*, 1686; 1908, **93**, 1559.

<sup>21</sup> *Ibid.*, 1908, **93**, 517.

existence of morphotropic relations, based on the considerations just put forward, are verified in actual practice

Whilst a large mass of results such as the above definitely prove the truth of the new crystallographic law of valency volumes, it is interesting that independent evidence establishing a relation between valency and volume has recently been brought forward from quite another source. G. Le Bas has shown<sup>22</sup> that the molecular volumes of a series of normal paraffins in the liquid state at the melting point can only be interpreted on the assumption that the atomic volume of carbon is four times that of hydrogen; the melting points are approximately equal fractions of the critical temperatures, and Le Bas has also demonstrated that the same relation holds in a series of paraffins when examined at some other series of corresponding temperatures. The molecular volumes,  $M$ , of the normal paraffins containing from 11 to 35, or  $n$ , carbon atoms in the molecule, in the liquid state at the melting point, are given by the expression:

$$M = 2.970(6n + 2) = 2.970 \text{ } IV :$$

$IV$  being the valency volume; the quantity 2.970 represents the atomic volume of hydrogen in the hydrocarbons under the conditions specified. Somewhat similar results have been obtained by I. Traube,<sup>23</sup> as regards the proportionality, not only of valency and atomic volume, but also of valency and atomic refraction. In a later paper,<sup>24</sup> Le Bas extends his conclusions to olefinic and acetylenic hydrocarbons.

The definite demonstration which Le Bas has furnished of the relation between the atomic volumes of hydrogen and carbon in liquid hydrocarbons and the valency of these two elements is of importance in connexion with the nature of liquids; it indicates that the principle of close packing of the molecular aggregates still applies in liquids, the main difference between the liquid and the crystalline states being probably that, whilst both are close-packed conditions, the latter is a structurally homogeneous state, and the former is not. Further, since in liquids the valency volume is only proportional to the molecular volume under corresponding conditions, it is suggested that throughout series of crystalline substances the molecular volumes would be proportional to the valency volumes if the former values could be determined at corresponding temperatures. No means of defining corresponding temperatures, in the sense of the van der Waals gas equation, for crystalline substances, are as yet available, but in the light of the results now

<sup>22</sup> *Trans.*, 1907, 91, 112; *Phil. Mag.*, 1907, [vi], 14, 324; *A.*, 1907, ii, 754.

<sup>23</sup> *Ber.*, 1907, 40, 723; *A.*, 1907, ii, 205.

<sup>24</sup> *Phil. Mag.*, 1908, [vi], 16, 60; *A.*, ii, 667.



reviewed it would seem likely that, measured at corresponding temperatures, the molecular distance ratios would be directly proportional to the equivalence parameters throughout series of crystalline substances. This probability seems likely to render unfruitful attempts to ascertain the nature of specific crystal structures by correlating the crystalline form, the atomic volumes of the component elements, and the changes in molecular volume which accompany polymorphous changes in the materials concerned. Much work of a very suggestive character has, however, been done on this subject by W. J. Sollas.<sup>25</sup>

As indicating the probability of the transient existence in liquids throughout molecularly large tracts of homogeneously arranged aggregates of molecules, the work of O. Lehmann, D. Vorländer, F. M. Jaeger, and others on the so-called "liquid crystals" may be quoted. A number of substances, many of which exhibit close constitutional relationships, are now known which throughout definite ranges of temperature exist in liquid phases exhibiting double refraction and other behaviour ordinarily attributed to crystalline structures; in certain cases the occurrence of dimorphism and of sudden changes of optical orientation can be distinctly observed.

As has been remarked above, the partitioning of a crystal structure into close-fitting polyhedral units, each of which represents the sphere of influence of a constituent atom, is equivalent to, and is conveniently replaced by, the building up of a system of spheres in contact with each other. The equilibrium condition—that the polyhedra shall assume shapes as nearly spherical as possible—is imitated by arranging the spheres in close-packing; that is to say, so that the assemblage presents the maximum number of contacts between spheres. If the assemblage of spheres is compressed from all sides so as to eliminate the interstices, each sphere becomes flattened to polyhedral shape.<sup>26</sup>

The construction of a model which shall represent in dimensions and structure the crystalline form of any given substance consequently resolves itself into the construction of a close-packed assemblage of spheres of volumes proportional to the fundamental valencies of the several elements contained in the substance, the proportion in which the various kinds of spheres are used being given by the molecular composition. The assemblage thus produced must be characterised by symmetry and translations identical with those of the crystalline substance, and must be capable of partition into units, each of which represents in composition, constitution, and configuration a chemical molecule. These conditions narrowly

<sup>25</sup> *Proc. Roy. Soc.*, 1898, **63**, 291.

<sup>26</sup> *Trans.*, 1907, **91**, 1157.

limit the possible assemblages of spheres which may be presented for any particular case.

The investigation of the case of benzene in the manner just indicated has led to the production of a model which is in accordance with the crystalline form of the hydrocarbon, and which may be partitioned into units, each of the composition  $C_6H_6$ , and possessing a definite configuration of a novel character.<sup>27</sup> The model of the benzene molecule thus derived accords with the general behaviour of the hydrocarbon, and possesses certain advantages over the older models; thus it shows how the ortho-para law of substitution operates, it indicates why optical activity is not exhibited by certain of the di-derivatives of benzene, and offers a very simple mechanism representing the production of benzene or its homologues from the corresponding acetylene derivatives.<sup>28</sup> In similar manner models representing naphthalene and anthracene have been devised. It should, perhaps, be emphasised that in constructing close-packed assemblages representing crystalline benzene or any other substance no suggestion is made that the component atoms are packed closely together; the close-packing of the spheres of atomic influence merely means that the whole of the space occupied by a crystalline material is occupied by the constituent atoms in the sense that any point chosen within it is subject to the predominant influence of some one atom and that each atom thus influences a domain which is approximately spherical in shape.

Two important questions relating to substitution and multivalency are conveniently considered in connexion with close-packed assemblages of the same or different sizes. Firstly, if, in a homogeneous and close-packed assemblage of spheres, homogeneously situated spheres each of volume  $m$  are each replaced by a group of two or more spheres having the total volume  $m$ , a slight distortion of the assemblage, which does not change the grouping of the unchanged spheres, suffices for the restoration of close-packing. This is termed the first geometrical property of close-packed homogeneous assemblages, and indicates that in the assemblages representing the crystal structures of substances of some molecular complexity, one kind of sphere of a certain magnitude may be replaced by several others of the same total magnitude, or vice versa, without necessitating any considerable rearrangement or "remarshalling" of the assemblage as a whole. It indicates, for instance, that if all the nitrogen spheres, each of volume 3, in the assemblage representing triphenylamine are replaced, each by three spheres of volume 1,

<sup>27</sup> *Trans.*, 1906, **89**, 1692.

<sup>28</sup> Compare J. B. Tingle and F. C. Blanck, *J. Amer. Chem. Soc.*, 1908, **30**, 1596; *A.*, i, 893.

representing hydrogen, close-packing can be restored to the modified assemblage by a slight distortion, which leaves the groups of spheres representing the phenyl radicles of unchanged configuration. The second point of importance arises in connexion with the so-called second geometrical property of close-packed homogeneous assemblages. This states that if, in such an assemblage as that of triphenylamine, the nitrogen spheres of volume 3 are each replaced by a carbon sphere of volume 4, close-packing can only be restored by distortion unaccompanied by remarshalling, if for each extra unit of volume thus added yet another extra unit of volume is introduced. So that if the nitrogen spheres are substituted by carbon spheres as just supposed, the restoration of the close-packing can only be brought about without profound rearrangement of the assemblage by introducing a sphere of volume 1 with each carbon sphere; the relations between the assemblages and the molecular compositions of triphenylamine and triphenylmethane are thus indicated. The modes in which substitutions, such as those of  $\text{:N}$  by  $\text{:CH}$ , or of  $\cdot\text{H}$  by  $\cdot\text{OH}$ ,  $\cdot\text{NH}_2$ ,  $\cdot\text{CH}_3$ , or  $\cdot\text{CN}$ , occur whilst some large radicle in the assemblage preserves its original configuration are thus elucidated.

The second geometrical property has, however, still wider applications. The replacement of the nitrogen sphere of volume 3 by the carbon sphere of volume 4 is, under the conditions explained, geometrically equivalent to introducing with it another sphere of volume 1, such as a hydrogen sphere; and by the same argument as before, it is necessary, in order to restore close-packing without remarshalling, to associate yet another sphere of volume 1 with the nitrogen sphere. By selecting a chlorine sphere of unit volume for the latter purpose a mode is indicated by which the assemblage for ammonia or an amine can be converted into ammonium chloride or one of its alkyl derivatives, and generally by which the valency of an element can be caused to increase by two, or a whole multiple of two, units.<sup>29</sup> Further, the application of the second geometrical property elucidates immediately the well-known relationship between the crystal forms of calcite,  $\text{CaCO}_3$ , and sodium nitrate,  $\text{NaNO}_3$ . The crystalline structures of those two substances are highly characteristic and present striking peculiarities; they are of identical symmetry and of almost the same relative dimensions, and yet no correspondence exists between calcium and carbon on the one hand, and sodium and nitrogen on the other. The second geometrical property indicates, however, that if the nitrogen spheres of volume 3 present in the sodium nitrate assemblage are replaced each by a carbon sphere of volume 4, an extra unit of volume must be introduced for each sphere so substituted in order that close-

<sup>29</sup> *Trans.*, 1907, 91, 1204.

packing may be re-established without remarshalling; the similarity between the two crystalline substances indicates that they have the same marshalling, and the extra unit of volume thus called for is introduced by, at the same time, replacing each sodium sphere of volume 1 by a calcium sphere of volume 2. Incidentally it is indicated that the molecules of calcium carbonate and sodium nitrate have the same configuration. The crystalline structures of these two rhombohedral substances have been worked out in detail,<sup>30</sup> as also have those of the similarly related but orthorhombic aragonite,  $\text{CaCO}_3$ , and potassium nitrate. Several other morphotropic relationships of similar kind have been recently discussed by F. M. Jaeger with the aid of the equivalence parameters.<sup>31</sup>

Comparatively few cases of morphotropic relationship between the several polymorphous modifications of any particular substance have been recorded, but by examining the crystalline forms of such compounds; under the aspects suggested by the new mode of regarding crystal structure, numerous analogies are revealed. The mode of occurrence of polymorphism is best illustrated by aid of a simple example. The cubic and hexagonal crystal structures of silver iodide have been imitated by the construction of cubic and hexagonal closest-packed systems of spheres of the same size; in these constructions equal numbers of triangularly-arranged layers of spheres of the same sizes are packed together in two alternative manners. The one kind of layer contains three times as many spheres representing silver atomic domains as of those representing iodine; the other kind of layer contains three times as many iodine as silver spheres. The arrangement of equal numbers of these two kinds of layers which gives the cubic closest-packed assemblage is one in which the layers are so stacked one upon the other that the fourth layer comes exactly over the first, the fifth over the second, and so on; in the hexagonal arrangement the layers are so stacked that the third lies over the first, the fourth over the second, and so on. The conversion of the cubic modification into the hexagonal one is equivalent to converting the cubic assemblage into the hexagonal one by sliding each third layer in the stack into the appropriate position. Both assemblages are capable of geometrical partition into identical units representing the molecule  $\text{AgI}$ , and so may be regarded merely as different modes of packing together identical molecular units. If this is correct, and if polymorphously related crystal structures are to be regarded as made up of identical layers packed together in alternative ways, it should, in general, be possible to determine identical sets of translations in the several such crystal structures. This selec-

<sup>30</sup> *Trans.*, 1908, 93, 1528.

<sup>31</sup> *Ibid.*, 517.

tion is obviously possible in the cubic and hexagonal assemblages presented for silver iodide, because the horizontal translations within the layers are the same in both cases, and the vertical translations or the distances between the planes of sphere centres in two adjoining layers, are also the same. The morphotropic relation thus indicated, namely, the possibility of calculating the axial ratios of one substance from those of a polymorphously related substance by some simple change in the axial directions, has been discovered in a number of instances. Thus, by merely changing the axial directions in the hemimorphously rhombohedral silver antimony sulphide,  $\text{Ag}_3\text{SbS}_3$ , for which Miers gives the values  $a:c=1:0.7892$ , axial ratios are obtained of the values  $a:b:c=1.9007:1:1.0974$ ,  $\beta=90^\circ$ ; these correspond closely with the axial ratios,  $a:b:c=1.9465:1:1.0973$ ,  $\beta=90^\circ$ , given for the monosymmetric mineral of the same composition.<sup>32</sup> Cases of isopolymorphism may be dealt with in the same way. Thus the transposition of the axial ratios,  $a:c=1:0.8276$ , of the rhombohedral sodium nitrate yields the axial ratios,  $a:b:c=1.7320:1:0.7151$ , values almost identical with those stated by Jaeger<sup>33</sup> for the orthorhombic rubidium nitrate, namely,  $a:b:c=1.7366:1:0.7106$ .

The treatment of crystal structures as close-packed assemblages and the interpretation of the crystal measurements by the aid of the equivalence parameters suggests wide developments of the whole subject of morphotropic relationships; one of these has been followed up with success. In the assemblage representing crystalline benzene and in those for the simple benzene derivatives, the carbon spheres are found arranged in columns; each joint in the latter consists of three carbon spheres arranged in triangular contact.<sup>34</sup> The presence of these columns keeps the translation measured in their direction the same in the various assemblages in which they occur; in benzene itself the value of this translation is that of the equivalence parameter  $z=2.780$ . It would consequently be expected that this value should occur amongst the equivalence parameters of any benzene derivative the assemblage of which contains the columns remarked. On calculating the equivalence parameters of twelve derivatives of picric and styphnic acids, it has been found that one of the three equivalence parameters in each case assumes a value closely approaching to the value  $z=2.780$ , for benzene.<sup>35</sup> The prediction as to the existence of this particular morphotropic relation has thus been amply verified, and an indication has been obtained that the

<sup>32</sup> *Trans.*, 1908, 93, 1531.

<sup>33</sup> *Zeitsch. Kryst. Min.*, 1907, 43, 588.

<sup>34</sup> *Trans.*, 1906, 89, 1693.

<sup>35</sup> G. Jerusalem and W. J. Pope, *Proc. Roy. Soc.* 1908 80, A, 557; *A.* ii, 674.

occurrence in the crystal structure of the columns of carbon spheres referred to is a general property of benzene derivatives. The interpretation to be placed upon the general occurrence of the columns is that, in the passage from crystalline benzene to some crystalline derivative, the columns of carbon spheres move apart to a sufficient extent to allow of the introduction of the substituting groups, the increase of volume thus rendered available for occupation by spheres of atomic influence being proportional to the increase in valency volume caused by the substitution.

The fixity of arrangement of part of the crystalline structure during changes amongst comparatively small substituting groups in large molecular complexes, as well as the operation of the first and second geometrical properties which are observed in the case of the above substances, is also well exemplified by the near approximation to identity of the axial ratios of dibenzyl, stilbene, tolane, and azobenzene.<sup>36</sup> The precision with which the changes of the equivalence parameters accord with the changes of composition in such series of related substances as the above proves definitely that the volumes of the spheres of atomic influence in any given compound are approximately proportional to the fundamental valencies of the elements concerned. This also involves the conclusion that when a considerable increase of molecular volume attends the substitution of one atom by another of the same valency, as, for example, the replacement of hydrogen by chlorine in benzene, each component sphere of atomic influence is proportionally enlarged; the volumes appropriated in the chlorobenzenes by hydrogen, chlorine, and carbon still stand in the ratio of their respective fundamental valencies, although those for hydrogen and carbon are actually greater than in benzene itself.

WILLIAM JACKSON POPE.

<sup>36</sup> Zirngiehl, *Zeitsch. Kryst. Min.*, 1902, **36**, 117; *A.*, 1902, ii, 496.



## INDEX OF AUTHORS' NAMES.

---

- |   |  |
|---|--|
| <p>             Abderhalden, E., 170.<br/>             Abegg, R., 24.<br/>             Abel, E., 49.<br/>             Acheson, E. G., 58.<br/>             Ackermann, F., 204.<br/>             Acree, S. F., 83, 184.<br/>             Adams, G. O., 197.<br/>             Adeney, W. E., 197.<br/>             Allmand, A. J., 45.<br/>             Alway, F. J., 250.<br/>             Andersen, A. C., 185.<br/>             Anschutz, R., 125.<br/>             Antoni, W., 206.<br/>             Antropoff, A. von, 48.<br/>             Archbutt, S. L., 187.<br/>             Armstrong, H. E., 21, 23.<br/>             Arthur, W., 191.<br/>             Astruc, H., 207.<br/>             Atkins, W. R. G., 208.<br/>             Aumer, J., 188.<br/>             Austin, P. C., 120.<br/>             Autenrieth, W., 193.<br/>             Auwers, K., 144, 145.<br/> <br/>             Baborovský, J., 48.<br/>             Baddiley, J., 112.<br/>             Badische Anilin- &amp; Soda-Fabrik, 67.<br/>             Baglioni, S., 256.<br/>             Bain, J. W., 188.<br/>             Baker, H. B., 38.<br/>             Baker, J. L., 208.<br/>             Balke, C. W., 51, 69.<br/>             Baly, E. C. C., 83, 132, 133.<br/>             Bamberger, E., 112.<br/>             Bancroft, W. D., 11.<br/>             Bang, I., 217, 219.<br/>             Barberio, M., 185.<br/>             Barger, G., 158, 172.<br/>             Barker, T. V., 264, 267.<br/>             Barlow, W., 268, <i>et seq.</i><br/>             Barr, G., 198.<br/>             Barr, W. M., 69.<br/>             Bartelt, K., 101.<br/>             Baskoff, A., 241.         </p> | <p>             Baubigny, H., 185.<br/>             Bauer, K., 238.<br/>             Bauer, O., 71.<br/>             Baume, G., 38.<br/>             Baur, E., 252.<br/>             Baxter, G. P., 38.<br/>             Bay, I., 201.<br/>             Beans, H. T., 195.<br/>             Beck, P., 188.<br/>             Becker, W., 70.<br/>             Behrend, R., 87.<br/>             Belloni, E., 200.<br/>             Bellucci, I., 56.<br/>             Bemberg, J. P., 89.<br/>             Bemmelen, J. M. van, 65.<br/>             Benda, L., 174.<br/>             Bennett, C. T., 204.<br/>             Berchem, O., 196.<br/>             Bereza, S., 85.<br/>             Berg, P., 90.<br/>             Bergmann, von, 208.<br/>             Berkeley, Earl of, 15, 16.<br/>             Berl, E., 89.<br/>             Berthelm, A., 174.<br/>             Bettel, W., 183.<br/>             Bevan, E. J., 205.<br/>             Beyer, F. B., 193.<br/>             Beyerinck, M. W., 242.<br/>             Bezdzik, A., 158.<br/>             Bienenfeld, B., 216.<br/>             Biginelli, P., 209.<br/>             Biltz, H., 40.<br/>             Biltz, W., 60.<br/>             Biquard, R., 62.<br/>             Birckenbach, L., 38.<br/>             Birschel, E., 128.<br/>             Blacher, C. J., 197.<br/>             Blackman, P., 200.<br/>             Blair, A. A., 191.<br/>             Blanck, F. C., 274, 275.<br/>             Bloch, A., 204.<br/>             Bloch, E., 68.<br/>             Bloch, I., 53.<br/>             Bloch, L., 68.         </p> |
|---|--|



- Blume, G., 201.  
 Bodmer, E., 161.  
 Bodtker, E., 81.  
 Boeseken, J., 81.  
 Bokman, G., 55.  
 Boters, O., 113.  
 Bogert, M. T., 118.  
 Bollenbach, H., 182, 190, 201.  
 Bolton, W. von, 44.  
 Bone, W. A., 84, 196.  
 Bongé, W. von, 89.  
 Bordas, F., 182.  
 Borelli, V., 57.  
 Borgmann, I., 97.  
 Borgo, A., 53.  
 Bornemann, K., 43.  
 Borsche, W., 119, 120, 143.  
 Rose, E., 105.  
 Bossuet, R., 42.  
 Bourguignon, A., 75.  
 Bourion, F., 193.  
 Bousfield, W. R., 196.  
 Bouveault, L., 102.  
 Bowen, J. L., 204.  
 Brand, J., 192.  
 Brandt, L., 189.  
 Brauner, B., 36.  
 Bray, W. C., 181.  
 Brdlik, V., 254.  
 Bredemann, G., 244.  
 Brieger, L., 208.  
 Briggs, J. F., 205.  
 Briner, E., 41, 50.  
 Brisbane, F. J., 45.  
 Brodie, T. G., 225.  
 Brown, C. W., 246.  
 Brown, H. T., 253.  
 Brown, P. E., 246.  
 Brown, T. G., 226.  
 Browne, A. W., 66.  
 Brühl, J. W., 100.  
 Brunck, O., 190.  
 Bruni, G., 53.  
 Brunner, H., 186.  
 Bruschi, D., 253.  
 Bryan, H., 206.  
 Buchner, E., 121.  
 Burrows, H., 196.  
 Burton, C. V., 16.  
 Busch, M., 80, 201.  
 Bush, G. C., 179.  
 Buttle, B. H., 186.  
 Cain, J. C., 112, 136, 137, 138.  
 Calcagni, G., 68.  
 Calhane, D. F., 181.  
 Callendar, H. L., 18.  
 Cambi, L., 56.  
 Camiola, G., 246.  
 Campbell, E. D., 191.  
 Cantoni, H., 190.  
 Carleton, P. W., 124.  
 Carlson, B., 186.  
 Caron, H., 181, 183.  
 Carpiaux, E., 254.  
 Carrasco, O., 200.  
 Cathcart, E. P., 226.  
 Cazeneuve, P., 191.  
 Cenni, G., 195.  
 Cesaris, P. de, 56.  
 Chace, E. M., 204.  
 Chalker, W. C., 54.  
 Chapman, A. C., 207.  
 Charpy, G., 41.  
 Charrier, G., 143.  
 Chattaway, F. D., 139.  
 Chemische Fabrik Griesheim-Elektron, 68.  
 Chemische Fabrik vorm. Goldenberg, Geromont & Co., 207.  
 Chesneau, G., 187.  
 Chick, Miss F., 85.  
 Chouchak, D., 257.  
 Christensen, P., 187.  
 Ciancian, G., 92.  
 Clark, H. W., 197.  
 Clark, R. H., 81.  
 Clarke, L., 185.  
 Clarke, R. W. L., 81.  
 Classen, A., 193.  
 Clayton, A., 147, 149.  
 Clough, G. W., 110.  
 Cobb, P. H., 90.  
 Coca, 237.  
 Cohen, E., 17, 40, 194.  
 Cohen, J. B., 113.  
 Coleman, L. C., 244.  
 Colman, H. G., 201.  
 Colman, J., 115.  
 Colson, A., 40, 51.  
 Commelin, J. W., 17.  
 Cone, L. H., 171.  
 Cook, T., 200.  
 Copaux, H., 46.  
 Coppadoro, A., 51.  
 Cordier, V. von, 201.  
 Corradi, R., 201.  
 Courtauld, R. M., 197.  
 Coward, H. F., 84.  
 Cramer, W., 222, 224, 235.  
 Crewdson, Miss M. S., 78.  
 Crookes, Sir W., 71, 195.  
 Cross, C. F., 205.  
 Cullis, Miss W. C., 225.  
 Curtius, T., 96.  
 Cushman, A. S., 62.  
 Dakin, H. D., 87, 198.  
 Damm, F., 44.  
 D'Ans, J., 63.  
 Darapsky, A., 96.  
 Darbishire, F. V., 250.

Danfresne, M., 204.  
 Decker, H., 126, 156, 168.  
 Defacqz, E., 46, 193.  
 Dehn, W. M., 198.  
 Delbruck, K., 121.  
 Delépine, M., 56, 183.  
 Dengler, O., 164.  
 Denham, H. G., 45, 56.  
 Denigès, G., 192, 199, 207.  
 Dennis, L. M., 197.  
 Dennstedt, M., 199, 200.  
 Desamari, K., 124.  
 Desch, C. H., 133, 189.  
 Deuss, J. J. B., 177.  
 Dieckmann, W., 82.  
 Diels, O., 85.  
 Dienstbach, O., 183.  
 Dumroth, O., 133, 142.  
 Dittrich, M., 192.  
 Donan, J., 184.  
 Dons, R. K., 203.  
 Dorée, C., 231, 233.  
 Dott, D. B., 191.  
 Dreyer, L., 209.  
 Drushel, W. A., 193.  
 Duboin, A., 60.  
 Duboux, M., 206, 207.  
 Duke, W. W., 225.  
 Dunant, G., 168.  
 Dungern, von, 237.  
 Duulap, E. E., 188.  
 Dunstan, A. E., 91, 111.  
 Dupont, E., 207.  
 Durand, E., 41, 50.  
 Dutoit, P., 206, 207.  
 Duyk, M., 192.

Ebler, E., 66, 181.  
 Eckardt, M., 144.  
 Eddy, E. A., 82.  
 Edgar, E. C., 37.  
 Edgar, G., 190, 193.  
 Edwards, W. H., 132.  
 Eggink, B. G., 45.  
 Einhorn, A., 85, 173.  
 Emerson, W. H., 203.  
 Emmerich, F., 100.  
 Engel, 216.  
 Engels, P., 153.  
 Ephraim, F., 43.  
 Erdmann, H., 39, 60, 63.  
 Erlandsen, A., 230.  
 Ernyei, E., 197.  
 Euler, H. von, 137.  
 Evans, Miss C. de B., 35.  
 Everatt, R. W., 105.  
 Ewart, A. J., 252.  
 Ewers, E., 202.  
 Ewins, A. J., 158, 172.

Fabris, U., 75.

Falcke, V., 53.  
 Falk, F., 239.  
 Farbwerke vorm. Meister Lucius and  
 Brüning, 172.  
 Favrel, G., 207.  
 Faworsky, A. E., 97.  
 Feilitzen, H. von, 254.  
 Feist, K., 169.  
 Felser, H., 156.  
 Fenton, H. J. H., 198.  
 Fichter, F., 128.  
 Fickewirth, G., 149.  
 Fierz, H. E., 94, 95.  
 Fillinger, F. von, 198.  
 Finnemore, H., 173.  
 Fischer, A., 195.  
 Fischer, E., 110, 170, 171.  
 Fischer, F., 49, 61.  
 Fischer, O., 162.  
 Fisher, K., 97, 98.  
 Fitzgerald, E., 82.  
 Fleig, C., 199, 204.  
 Fletcher, F., 249.  
 Flurschein, B., 113.  
 Foerster, F., 67, 193, 194.  
 Fokin, S., 203.  
 Foote, H. W., 44, 54.  
 Ford, J. S., 207, 208.  
 Formhals, R., 191.  
 Forster, M. O., 94, 95, 101.  
 Fox, J. J., 147.  
 Fraenckel, A., 196.  
 Fraenkel, W., 42.  
 Frank, A., 206.  
 Franzen, H., 197.  
 Free, E. E., 194.  
 Friedlander, P., 158.  
 Friedrich, K., 42.  
 Friend, J. N., 32, 64, 71.  
 Fries, K., 147, 149.  
 Fröhlich, H., 244.  
 Fromm, E., 178.  
 Furth, O. von, 219, 238.  
 Fuld, E., 216.  
 Funaro, R., 228.

Gabriel, S., 114, 115.  
 Gain, G., 69.  
 Galletly, J. C., 65.  
 Gallo, G., 195.  
 Gardner, J. A., 231, 233.  
 Garnier, L., 199.  
 Gaubert, P., 63.  
 Gawalowski, A., 196.  
 Gazdar, Miss M., 177.  
 Gebhard, N. L., 196.  
 Geerligs, H. C. P., 202, 206.  
 Gelhaar, J., 186.  
 Gemmell, W., 187.  
 Gernez, D., 13.  
 Gerum, J., 58, 76.

- Gewin, J. W. A., 217.  
 Gibson, B. J. H., 252.  
 Gillett, H. W., 194.  
 Gilmour, R., 87.  
 Gimingham, C. T., 245.  
 Glikin, W., 231.  
 Glover, W. H., 101, 102.  
 Gotz, C., 111.  
 Goldbaum, J. S., 195.  
 Goldemann, J., 128.  
 Goldschmidt, R., 195.  
 Golodetz, L., 198.  
 Gomborg, M., 135.  
 Gooch, F. A., 193.  
 Gorslue, E. E., 81.  
 Gortner, R. A., 175.  
 Gottlieb, R., 226.  
 Gowing-Scopes, L., 207.  
 Grammling, F., 56.  
 Grandmougin, E., 161.  
 Grazia, S. de, 246.  
 Green, A. G., 112, 184.  
 Greenwood, H. O., 44.  
 Grégoire, A., 254.  
 Gregory, A. W., 183, 190.  
 Grossmann, H., 182, 190.  
 Grube, K., 224.  
 Grzeschik, T., 188.  
 Guggenheim, M., 171.  
 Gurbier, A., 38, 56.  
 Guthrie, J. M., 207, 208.  
 Gutmann, A., 177.  
 Guttman, A., 45.  
 Gyr, J., 83.  
 Haakh, H., 107.  
 Haber, F., 67.  
 Hackspill, L., 42.  
 Haeffner, K., 94.  
 Haehn, H., 183.  
 Hahn, A., 79.  
 Haitinger, L., 64.  
 Halban, H. von, 109.  
 Haldane, J. S., 221.  
 Hall, A. D., 245, 255.  
 Hammarsten, O., 217.  
 Hamonnet, J. L., 79.  
 Hâncu, V. H., 91, 200.  
 Hannig, E., 244.  
 Hantzsch, A., 10, 133, 134, 136, 138, 184.  
 Hanuš, J., 204.  
 Harries, C. D., 93, 94, 99, 102.  
 Harrison, T. W., 189, 203.  
 Hartley, E. G. J., 15, 16.  
 Hartley, H., 26.  
 Hartmann, M., 142.  
 Hassler, F., 200.  
 Hauser, O., 192.  
 Haworth, W. N., 98.  
 Hay, J. G., 118.  
 Hedley, E. P., 133.  
 Hehner, O., 189.  
 Heikel, G., 201.  
 Heilborn, W., 182.  
 Heller, G., 80, 112.  
 Henderson, G. G., 65.  
 Hendrick, J., 254.  
 Henle, F., 107.  
 Herr, V. F., 201.  
 Herrmann, W., 109.  
 Herschmann, F., 118.  
 Hertzy, C. H., 204.  
 Herz, W., 45.  
 Herzig, J., 200.  
 Herzog, J., 200, 201.  
 Hesse, A., 79.  
 Heubner, W., 236.  
 Hewitt, J. T., 146, 147, 184, 186.  
 Heyn, E., 71.  
 Hiesstand, O., 253.  
 Hildebrand, J. H., 69, 185.  
 Hilditch, T. P., 105, 166, 178, 179.  
 Hill, A. E., 196, 199.  
 Hill, J. R., 105.  
 Hilscher, F., 134, 184.  
 Hinkel, F. C., 202.  
 Hinkel, L. E., 198.  
 Hinrichsen, F. W., 187, 193.  
 Hinsberg, O., 177.  
 Hirsowski, A., 170.  
 Hohn, F., 53.  
 Holland, W. W., 14.  
 Holmberg, B., 177.  
 Holmes, H., 101.  
 Holmes, Miss, M. E., 194.  
 Hoogenhuyze, C. J. C., van, 227.  
 Hopkins, F. G., 256.  
 Houben, J., 79.  
 Howell, W. H., 225.  
 Hubbard, P., 62.  
 Huber, L., 116.  
 Hubert, A., 207.  
 Hudson, C. S., 87.  
 Hugouenq, L., 171.  
 Hulton, H. F. E., 208.  
 Huntington, A. K., 189.  
 Hutchinson, G. A., 26.  
 Ilievici, G., 61.  
 Ingle, H., 203.  
 Ipatieff, W. N., 76.  
 Irvine, J. C., 87.  
 Isaac, Miss F., 26.  
 Isham, H., 188.  
 Jaboulay, E., 187.  
 Jackson, C. L., 124, 185.  
 Jacobson, P., 116.  
 Jacoby, J., 197.  
 Jacoby, M., 216.

Jaeger, F. M., 272, 277, 278.

Jakowleff, W., 76.

James, C., 60.

Jamieson, G. S., 189.

Jamieson, J. S., 184.

Jannasch, P., 185.

Jatar, S. B., 190.

Jeancaud, P., 204.

Jerusalem, E., 219.

Jerusalem, G., 278.

Jessen-Hansen, H., 205.

Jessup, A. C., 1.

Jessup, A. E., 1.

Jochheim, H., 157.

Johnson, O. M., 188.

Johnson, F. M. G., 24, 25.

Johnson, W. A., 208.

Johnston, S. M., 20.

Jones, B. M., 26.

Jones, G. C., 203.

Jones, H. C., 24.

Jones, H. O., 105.

Jones, W., 219.

Just, J., 254.

Kahan, Miss Z., 192.

Kahlenberg, L., 192.

Kahn, R., 174.

Kajura, S., 238.

Kantorowicz, H., 175.

Karpinski, A., 245.

Karslake, W. J., 183.

Kaufmann, H., 7, 9, 180, 135.

Kay, F. W., 171.

Keane, C. A., 196.

Kehrmann, F., 125, 126, 162, 163, 164.

Keiser, E. H., 64, 67, 196.

Keller, O., 167.

Kellner, O., 256.

Kenner, G. I., 38.

Kemp, R., 52.

Kendall, E. C., 199.

Kenner, J., 177.

Keppeler, G., 69.

Khotinsky, E., 176.

Kilian, H., 88, 187.

Kimball, A. W., 197.

Kipping, F. S., 175.

Kirpal, A., 200.

Klaber, W., 118.

Kleinschmitt, A., 256.

Klever, H. W., 84.

Klostermann, W., 147.

Knecht, E., 183.

Knoevenagel, E., 177.

Knorr, L., 168.

Knorre, G. von, 187, 193.

Kober, P. A., 196.

Koch, H., 188.

Koch, M., 67.

Koenig, A., 67.

Koeniger, P., 158.

Kotz, A., 111.

Kot, K., 183.

Kohn-Abrest, E., 196.

Komppa, G., 102.

Komnick, L. L. de, 188.

Kolb, A., 191.

Koppel, J., 33.

Kostanecki, S. von, 149, 154.

Kramel, A., 171.

Krafft, F., 44.

Kraus, C. A., 66.

Krauskopf, F. C., 192.

Krauss, I., 199.

Kreutz, A., 208.

Krou, A., 82.

Kropp, W., 171.

Kruyt, H. R., 39.

Kizemienewski, S., 243.

Kubli, H., 113.

Kuhn, G., 59.

Kuhn, O., 189.

Kuzma, B., 48.

Laar, C., 89.

Laar, J. J. van, 24.

Ladenburg, A., 109.

Lalin, L., 85.

Lampe, V., 154.

Lander, G. D., 182.

Landolt, H., 3.

Lang, W. R., 175, 189.

Lapworth, A., 81, 82.

Law, D. J., 89.

Law, H. D., 111.

Lawroff, D., 218.

Leather, J. P., 197.

Leather, J. W., 251.

Le Bas, G., 273.

Lebeau, P., 42, 44.

Le Chatelier, H., 65.

Lederer, R., 238.

Leeffhelm, L., 80.

Lefebvre, C., 198.

Lefmann, G., 228.

Lehmann, O., 274.

Leithauser, G., 67.

Lenher, V., 37, 187.

Lenz, W., 199.

Le Pla, Miss M., 188.

Le Rossignol, R., 177, 178.

Leroux, A., 42.

Leuchs, H., 168.

Levallois, 102.

Levene, P. A., 217, 218, 219.

Levi, M. G., 52.

Levy, H. L., 189.

Lewis, G. N., 20.

Lewis, W. C. M., 30.

Lewkowitsch, J., 203.

Ley, H., 132.

- Lidoff, A. P., 184.  
 Liebermann, C., 121, 122.  
 Liebig, H. von, 131.  
 Lifschutz, I., 198, 199.  
 Lilienfeld, L., 157.  
 Linck, G. E., 40.  
 Linder, E., 185.  
 Lang, A. R., 202, 203.  
 Lintner, C. J., 202, 208.  
 Lipman, J. G., 244, 246.  
 Liversedge, S. G., 188.  
 Lochhead, J., 244.  
 Locke, F. S., 225.  
 Lockemann, G., 191.  
 Lob, W., 88.  
 Lohnis, F., 243.  
 Lohmann, A., 238.  
 Lohr, F., 87.  
 Loose, R., 185.  
 Lowry, T. M., 89.  
 Luppe-Cramer, 58.  
 Luff, B. D. W., 175.  
 Luther, R., 47.  
 Lutz, O., 184.  
 Lyons, A. B., 185.  
 Lyons, R. E., 179.  
  
 McCarthy, E. S., 197.  
 McDonald, D. P., 108.  
 McKay, L. W., 182.  
 McKenzie, A., 109, 110.  
 Mackenzie, J. E., 53.  
 Mackey, J. F., 175.  
 MacLean, H., 238, 241.  
 McMaster, L., 67, 196.  
 McMillan, A., 93.  
 Magson, E. H., 89.  
 Mai, C., 206.  
 Mailhe, A., 75.  
 Main, H., 206.  
 Maire, M., 116.  
 Majima, R., 99.  
 Mameli, E., 252.  
 Mamlock, L., 167.  
 Manchot, W., 64, 65.  
 Mandel, J. A., 199, 218, 219.  
 Manca, A., 199.  
 Mannich, C., 91.  
 Mannelli, C., 62.  
 Marekwald, W., 37.  
 Marie, C., 71.  
 Marino, L., 47.  
 Marsden, Miss E. G., 83.  
 Marshall, H., 53.  
 Martin, F., 46.  
 Mathers, F. O., 64, 190.  
 Matthaiopoulos, G. T., 205.  
 Matthei, H., 203, 204.  
 Mauriceau-Beaupré, 62.  
 Mayer, E. W., 76.  
 Maxwell, S. S., 223.  
  
 Mdivani, B., 193.  
 Mears, B., 14.  
 Meisenheimer, J., 88, 109.  
 Meldola, R., 84, 118.  
 Meldrum, A. N., 86.  
 Mellanby, E., 226.  
 Mellet, R., 186.  
 Melzer, W., 176.  
 Mémère, P., 196.  
 Metzger, F. J., 195.  
 Meyer, F., 63.  
 Meyer, K., 203.  
 Meyer, K. H., 126.  
 Meyer, R., 124.  
 Meyer, R. J., 44.  
 Michael, A., 90.  
 Michaelis, A., 167, 174.  
 Mickelthwait, Miss F. M. G., 136, 174.  
 Mighoiini, E., 52.  
 Miers, H. A., 278.  
 Milbauer, J., 184.  
 Miller, I., 190.  
 Miller, N. H. J., 245.  
 Miller, O., 89.  
 Mills, W. H., 146.  
 Minz, A., 234.  
 Miolati, A., 54, 56.  
 Mitchell, A. D., 145.  
 Modrakowski, G., 239.  
 Moller, P., 40.  
 Mohr, O., 206.  
 Moir, J., 183.  
 Molinari, E., 93, 94.  
 Molz, E., 254.  
 Moodie, Miss A. M., 87.  
 Moore, C. W., 117.  
 Moore, E. P., 188.  
 Moore, R. B., 38, 61, 190.  
 Morel, A., 171.  
 Morgan, G. T., 136, 174, 200.  
 Morse, H. N., 14, 15.  
 Morse, H. V., 14.  
 Moureu, C., 62, 169.  
 Muggs, O., 65.  
 Müller, Ernst, 96.  
 Müller, F., 123.  
 Muller, G., 196.  
 Muir, M. M. P., 189.  
 Murphy, A., jun., 90.  
 Murschhauser, H., 46.  
  
 Nelken, F., 80.  
 Nerkin, J., 237.  
 Neuberg, C., 59, 88, 199.  
 Neumann, W., 182.  
 Newton, H. D., 189.  
 Nicolardot, P., 190, 193.  
 Nieuwland, C. H., 191.  
 Niklewski, B., 245.  
 Noeltung, E., 165.  
 Noll, H., 197.

- Noyes, A. A., 181.  
 Noyes, W. A., 36, 37.  
 Oddo, B., 79.  
 Oehler, E., 52.  
 Ogawa, M., 35.  
 Ogier, J., 196.  
 Olie, J., 40.  
 Onnes, H. K., 60.  
 Opoloski, S., 133.  
 Orloff, N. A., 183.  
 Orthey, M., 187, 188, 192.  
 Orton, K. J. P., 83, 92, 127.  
 Osborne, R. W., 82.  
 Osborne, T. B., 256.  
 Ostionusslensky, I. von, 91, 107.  
 Ott, E., 85.  
 Ozorovitz, N., 198.  
 Paal, C., 58, 59, 76.  
 Padua, M., 75.  
 Palmer, H. E., 82.  
 Panzer, T., 232.  
 Parnas, J., 123.  
 Parr, S. W., 186, 200.  
 Parravano, N., 68.  
 Parrozzani, A., 253.  
 Pascal, P., 56, 58.  
 Paschke, F., 109.  
 Patten, A. J., 246.  
 Patterson, T. S., 93, 108.  
 Pavy, F. W., 222.  
 Pawlewski, B. von, 198.  
 Pearson, Miss C., 92.  
 Pedrina, S., 43.  
 Pellini, G., 43.  
 Peltner, E., 50.  
 Perkin, F. M., 63, 111, 189, 193, 203.  
 Perkin, W. H., jun., 97, 98, 106, 152, 153, 156.  
 Perotti, R., 246.  
 Perrot, F. L., 38.  
 Peset, J., 195.  
 Peters, F., 147.  
 Pfeiffer, P., 54.  
 Pfluger, E., 224.  
 Phelps, I. K., 82.  
 Phelps, M. A., 82.  
 Philip, J. C., 95.  
 Philipoff, O., 76.  
 Philipp, K., 165.  
 Piccard, J., 125.  
 Pickering, S. U., 250.  
 Pickles, S. S., 100, 205.  
 Pieszczek, E., 188.  
 Pillai, N. K., 243.  
 Pizzighelli, R., 54, 56.  
 Plimmer, R. H. A., 205, 213.  
 Pokorný, F., 47.  
 Pollacci, G., 252.  
 Pollard, W. B., 181.  
 Ponzio, G., 143.  
 Pope, F. G., 135.  
 Pope, W. J., 106, 268 *et seq.*, 278.  
 Popielski, L., 238.  
 Popp, M., 255.  
 Porcher, C., 209.  
 Porter, A. W., 18.  
 Potdar, G. N., 62.  
 Potter, M. C., 246.  
 Pouget, I., 257.  
 Pozzi-Escot, M. E., 182, 190, 207.  
 Prandtl, W., 46.  
 Pratt, L., 63.  
 Price, T. S., 53, 176, 177.  
 Priestley, J. H., 252.  
 Pringle, H., 222.  
 Pritze, M., 68.  
 Purvis, J. E., 197.  
 Pyman, F. L., 172, 174.  
 Raabe, F., 168.  
 Raabe, O., 48.  
 Raabe, P., 90, 168.  
 Raben, E., 187.  
 Race, J., 206.  
 Raffo, M., 57.  
 Rakitin, L., 76.  
 Ramsay, Sir W., 4, 32, 61.  
 Raquet, D., 181, 183.  
 Raschig, F., 66, 201, 205.  
 Rassow, B., 89.  
 Read, J., 106.  
 Reckleben, H., 68, 191.  
 Recoura, A., 59.  
 Reed, H. S., 248.  
 Reichard, C., 199.  
 Reif, G., 171.  
 Rendle, T., 202.  
 Repiton, F., 187.  
 Rewald, B., 59.  
 Reyckler, A., 79.  
 Reynolds, H., 70, 191.  
 Reynolds, W. C., 174.  
 Richardson, F. W., 204.  
 Richmond, H. D., 200, 208.  
 Rimele, E., 96.  
 Ringe, O., 49.  
 Roaf, H. E., 205.  
 Robertson, T. B., 29.  
 Robinson, R., 152, 153, 156.  
 Robison, R., 175.  
 Rotgers, K., 44.  
 Rohdich, O., 203.  
 Rohland, P., 251.  
 Rolle, J., 167.  
 Romyn, G., 197.  
 Rorive, F., 199.  
 Rosenheim, A., 33, 68.  
 Rosenheim, O., 225, 233, 235.  
 Rosenstein, M., 190.  
 Rosenthaler, L., 191.

- Ross, R., 197.  
 Rotarski, T., 104.  
 Roth, K., 76.  
 Rothenfusser, S., 206.  
 Rothmann, A., 227.  
 Rowell, H. W., 192.  
 Rudolf, L., 112.  
 Ruer, R., 71.  
 Ruff, O., 176.  
 Rupe, H., 100.  
 Rupp, E., 185, 188.  
 Russell, E. J., 250.  
 Ryn, W. van, 192.  
 Sabatier, P., 75.  
 Sacher, J. F., 188.  
 Sachs, F., 175.  
 Sackett, W. G., 246.  
 Saito, K., 197.  
 Salkowski, E., 192, 233.  
 Sand, H. J. S., 194.  
 Sand, J., 55, 56.  
 Satie, C., 204.  
 Sawjaloff, W. W., 217.  
 Scala, A., 217.  
 Schaefer, K., 83.  
 Scharfenberg, W., 191.  
 Scharf, E., 67.  
 Scheen, O., 194.  
 Scheffer, F. E. C., 26.  
 Scheibler, H., 110, 171.  
 Schenck, R., 53.  
 Schindler, E., 162.  
 Schirmer, W. F., 188.  
 Schlenk, W., 126.  
 Schluederberg, C. G., 64.  
 Schmidlin, J., 135.  
 Schmidt, J., 168.  
 Schmiedeberg, O., 218.  
 Scholl, R., 160.  
 Scholtz, M., 109.  
 Scholz, H. A., 181.  
 Schoorl, N., 183.  
 Schorigin, P., 79.  
 Schott, E., 66.  
 Schrefeld, O., 202.  
 Schreiner, O., 247, 248.  
 Schück, B., 182, 190.  
 Schulke, K., 80.  
 Schürmann, E., 191.  
 Schugowitsch, A., 185.  
 Schulz, F., 199.  
 Schulze, K., 253.  
 Schumann, A., 195.  
 Schumann, T., 56.  
 Schwalbe, C. G., 157.  
 Schwarz, C., 238.  
 Schwarzenbach, R., 162.  
 Scott, F. H., 205, 213, 221.  
 Scott, S. F., 198.  
 Seurti, F., 253.  
 Selvatici, E., 182.  
 Semmler, F. W., 100, 101, 103.  
 Senderens, J. B., 77.  
 Seregenkoff, B., 176.  
 Shaffer, P. A., 228.  
 Sherman, H. C., 199, 202.  
 Shetterly, F. F., 66.  
 Shinn, O. L., 193.  
 Shorey, E. C., 247.  
 Shukoff, I. I., 65.  
 Sidgwick, N. V., 9.  
 Silber, P., 92.  
 Silbermann, T., 198.  
 Simon, T., 113.  
 Simons, H., 80, 147.  
 Sjollesma, B., 191.  
 Slade, R. E., 45.  
 Slyke, D. D. van, 217.  
 Smiles, S., 166, 177, 178, 179.  
 Smillie, R., 82.  
 Smussen, H. van der, 63.  
 Smith, Miss A. E., 83, 127.  
 Smith, C., 145.  
 Smith, E. F., 51, 69, 195.  
 Smith, E. K., 44.  
 Smith, H. D., 90.  
 Smith, J. L., 232.  
 Smith, W., jun., 89.  
 Smits, A., 26.  
 Snyder, C. D., 223.  
 Soderbaum, H. G., 246.  
 Soll, J., 168.  
 Sorensen, S. P. L., 185, 205.  
 Sourlis, A., 112.  
 Spear, E. B., 49, 181.  
 Spencer, J. P., 78, 188.  
 Spindler, O. von, 196.  
 Stangassinger, R., 226.  
 Stark, J., 6.  
 Staudinger, H., 84, 85, 86.  
 Steensma, F. A., 198.  
 Sallas, W. J., 270, 274.  
 Steiger, G., 186.  
 Stekl, L., 204.  
 Stern, K. L., 163.  
 Steudel, H., 219.  
 Stewart, A. W., 110, 132.  
 Stieglitz, J., 83, 184.  
 Stine, C. M., 24.  
 Stobbe, H., 92.  
 Stock, A., 68, 196.  
 Stokes, Miss E. M., 78.  
 Stoklasa, J., 243, 254.  
 Stoward, F., 253.  
 Strakosch, S., 252.  
 Stremme, H., 59.  
 Strengers, T., 40.  
 Strohmmer, F., 252.  
 Stubbs, J. A., 91.  
 Stutzer, A., 253.  
 Süchting, H., 196.

Sullivan, M. X., 248  
Sutherst, W. F., 254.  
Suzuki, U., 253.  
Sy, A. P., 203.

Takaki, K., 235.  
Tambor, J., 150  
Tammann, G., 42.  
Tebb, Miss M. C., 233, 235.  
Telle, F., 197.  
Tempany, H. A., 202, 203.  
Theodor, H., 189.  
Thiel, A., 194.  
Thiele, J., 66.  
Thorner, W., 208.  
Thole, F. B., 111  
Thomas, V., 79.  
Thompson, K. J., 138  
Thomson, D., 108.  
Thorpe, J. F., 117.  
Threlfall, R., 40.  
Tiffeneau, M., 92  
Tilden, W. A., 71.  
Tingle, J. B., 81, 274, 275.  
Tizard, H. T., 9.  
Tollens, B., 199.  
Tollens, K., 199.  
Traube, I., 273.  
Treadwell, W., 194.  
Trebing, J., 208.  
Trevor, J. E., 18  
Trivelli, A. P. H., 59  
Tschelinzoff, W., 78.  
Tschitschubabin, A. E., 129, 135  
Tschugaeff, L., 110, 182.  
Tsujiimoto, M., 203.  
Tuck, W. B., 133, 145.  
Turner, A. K., 204.  
Turner, M. R., 156.  
Turrentine, J. W., 52.  
Tutin, F., 100.  
Tutton, A. E. H., 264, 265, 266.  
Twiss, D. F., 53, 176, 177.

Uchiyama, S., 254.  
Ulrich, K., 64.  
Urbain, G., 34.  
Usher, F. L., 252.  
Utz, F., 201.

Valeur, A., 169.  
Vanino, L., 179.  
Vegard, L., 15.  
Veit, T., 66.  
Veley, V. H., 185.  
Venditori, D., 186.

Verploegh, H., 227.  
Vieweg, W., 89.  
Vogel, R., 42.  
Voley-Boucher, 198  
Voorhees, E. B., 246.  
Vorlander, D., 104, 274.

Wagner, M., 254.  
Walden, P., 26.  
Walden, P. T., 44.  
Waldmuller, M., 91.  
Wallace, Miss M. L., 78.  
Wallach, O., 100, 101, 102.  
Walton, J. H., jun., 181.  
Warburg, E., 67  
Warynski, T., 193.  
Washburn, E. W., 20.  
Wassilheff, N., 253.  
Watts, F., 202, 203.  
Weber, H. C. P., 37.  
Wechsler, E., 81.  
Wedekind, E., 66, 108, 109  
Wedekind, O., 108, 109.  
Wegscheider, R., 25, 185.  
Weichhold, O., 110.  
Weinland, R. F., 56.  
Weinmann, P. P. von, 59.  
Wells, H. L., 189.  
Welsbach, C. A. von, 34.  
Wenglein, O., 202.  
Werner, A., 55, 121, 122.  
Wheeler, E., 23.  
Wheeler, R. V., 196.  
White, C. P., 232, 233.  
Whymper, R., 24  
Widdows, Miss S. T., 146.  
Widemann, M., 188  
Willcock, Miss E. G., 256  
Willstätter, R., 76, 113, 123, 124, 125,  
254.  
Wilsmore, N. T. M., 85.  
Wilson, J. H., 38.  
Wilson, R. A., 235.  
Windisch, W., 253.  
Winiwarter, E. von, 188.  
Winter, H. W., 182.  
Winterstein, E., 253.  
Winterstein, H., 223.  
Wirth, F., 60, 192.  
Wislicenus, W., 90, 91.  
Withrow, J. R., 194.  
Witzmann, W., 44, 72.  
Wohler, L., 44, 46, 69, 70, 72  
Wohler, P., 44.  
Wohl, A., 86.  
Wohlgemuth, J., 207, 216.  
Wolffenstein, R., 50, 113, 167.  
Wolter, L., 65, 193.  
Wood, J. K., 185.



- |                        |                     |
|------------------------|---------------------|
| Woodhams, E. L., 191.  | Zaleski, J., 199    |
| Woodhouse, J. O., 189. | Zehenter, J., 200.  |
| Woolley, W. J., 224.   | Zeltner, J., 78.    |
| Wondstra, H. W., 188.  | Zengheis. C., 4     |
| Wien, H., 109.         | Zerewitnoff, T., 77 |
| Wyrouboff, G. N., 64.  | Zincke, T., 128.    |
| Yoshimura, K., 253.    | Zwayer, F., 149.    |

## INDEX OF SUBJECTS.

---

- Absorption spectra, 83.  
  of hydrocarbons, 131.  
  of nitro- and nitroso-compounds, 133.  
Acetylation of amino-groups, 83.  
Acridines, synthesis of, 119.  
Activity, optical, 105.  
Adrenaline, 238.  
Adsorption, 29.  
Alcohol, estimation of, in wine, 206.  
Aldebaranium, 34.  
Alizarin, production of, 114.  
Alkali metals, separation of, 195.  
Alkaloids, 167.  
  reactions of, 199.  
Allotropy of elements, 38.  
Alloys, 41.  
Alumina as catalyst, 77.  
Amido-myeelin, 240.  
Aminoazo-compounds, salts of, 134.  
Ammonium chloride, dissociation of, 24.  
  halides, crystalline structure of, 265.  
  iodide, equilibrium pressure of, 25.  
  persulphate, use of, in analysis, 182.  
Anaesthetics, 171.  
Analysis, elementary organic, 199.  
Antimony, estimation of, 191, 194.  
Apocynin, synthesis of, 173.  
Aqueous solutions, 20.  
Aragonite, crystalline form of, 277.  
Argon group, 60.  
Aromatic compounds, production of,  
  from hydroaromatic compounds, 111.  
  substances, oxidation of, 111.  
Arsenic, estimation of, 191.  
  modifications of, 39.  
  organic derivatives of, 173.  
Arsine, reactions of, 68.  
Asymmetric synthesis, 106.  
Atmosphere, gases of the, 61.  
Atomic weights, 36.  
Atropine, synthesis of, 167.  
*apo*Atropine, synthesis of, 167.  
Aurates, preparation of, 63.  
  
Axial ratios, 259.  
Azines, 161.  
Azoinide, preparation of, 66.  
Azomethines, 134.  
*Azotobacter*, nutrition of, 243  
  
Bacteriology of soil, 242.  
Barium, detection and separation of,  
  183.  
  separation of, from strontium, 192.  
  percarbonate, 50.  
  sulphate, colloidal, 59.  
Barley, biochemistry of, 207.  
Benzene, crystalline structure of, 275.  
Benzeneazo- $\alpha$ -naphthol, *p*-nitro-, use of,  
  as indicator, 184.  
Benzoin, preparation of two optically  
  active forms of, 109.  
Bismuth, atomic weight of, 38.  
  estimation of, 192, 195.  
Bistriazoacetic acid, ethyl ester of, 95.  
Bistriazo-compounds, 95.  
Bistriazoethane, 95.  
Boiling point, 28.  
  elevation of, 19.  
Brazan, synthesis of, 153.  
Brazilein, constitution of, 152.  
Brazilin, 150.  
Brazilinic acid, synthesis of, 152.  
Bromides, test for, 184.  
  
Cadmium, electrolytic separation of,  
  194.  
Calcite, crystalline form of, 276.  
Calcium, properties of metallic, 63.  
  bicarbonate, 64.  
  ferrocyanide, vapour pressure and  
  osmotic pressure of solutions of,  
  16.  
  hypochlorite, preparation of dry, 70.  
  sulphate, double salts from, 63.  
Camphor, synthesis of, 102.  
  isonitroso-, 101.  
Carbohydrates, 87.

- Carbon, determination of, in soils 257.  
 estimation of, 187.  
 in iron and steel, 188.  
 monoxide, absorption of, by cuprous chloride solution, 64.  
 estimation of, in air, 196.  
 suboxide, 85.  
 Carboxonium dyes, 163.  
 Carvenene, 99.  
*iso*Carvestrene, synthesis of, 97.  
 Caseinogen, 215.  
 Cassiopeium, 34.  
 Catalysis, 74, 82.  
 Cellulose, 88.  
 Cerebrosides, 231.  
 Cerium, estimation of, 192.  
 Chlorates, estimation of, 186.  
 Chlorine, action of silent electric discharge on, 41.  
 atomic weight of, 37.  
 Chlorites, detection of, 186.  
 Chlorophyll, 254.  
 Chlorosis, 254.  
 Cholesterol, 231.  
 Choline, 237.  
 Chortosterol, 234.  
 Chromium, complex salts of, 56.  
 detection of, 183.  
 estimation of, 190.  
 Cinchonine, constitution of, 168.  
 Cinchoninone, constitution of, 168.  
 Citric acid, detection of, 207.  
 Claisen condensation, the, 31.  
 Cobalt, complex salts of, 55.  
 detection of, 182.  
 estimation of, 190.  
 Cobra venom, 234.  
 Cohesion, specific, 27.  
 Colloids, 57.  
 Colour reactions, 198.  
 and constitution, 130.  
 lakes, 121.  
 of salts in solution, 9.  
 Colours, mordant, 121.  
 Columba root, alkaloids of, 169.  
 Columbamine, 169.  
 Columbium and its compounds, 51.  
 Complex salts, 54.  
 Conduction, rate of, in nerve, 223.  
 Constitution, 31, 32.  
 and colour, 130.  
 Copper, detection of, 183.  
 estimation of, 189, 194.  
 Coumarin, constitution of, 149.  
 group, the, 147.  
 Coupling, mechanism of, 141, 142.  
 Creatine, 226.  
 Creatinine, 226.  
 Crystalline structure, 258.  
 Crystals, liquid, 274.  
 structure of, 258.  
 Cuorin, 241.  
 Damascenine, constitution of, 167.  
 Desmotropy, 90.  
 Dextrose solutions, osmotic pressure of, 15.  
 Diamond, crystalline structure of 270.  
 Diazo-compounds, aliphatic, 94.  
 aromatic, 136.  
 Diazo-salts, constitution of, 136.  
 decomposition of, 137.  
 preparation of, 139.  
 Dielectric constants, 110.  
*p* - Dimethylaminoazobenzene - *o* - carboxylic acid, use of, as indicator, 185.  
 $\alpha$ -Dioximes, determination of configuration of, 110.  
 Diphenanthracendine, synthesis of, 120.  
 Dissociation pressures, abnormal, 24.  
 Electrochemical analysis, 193.  
 Electrochemistry, 11.  
 Electronic theory, 4.  
 Electrons, 2.  
 Elements, allotropy of, 38.  
 evolution of the, 1.  
 new, 34.  
 Elemenin, 103.  
 Ethyl tartrate, influence of solvents on optical activity of, 108.  
 Esterification, 82.  
 rate of, of acids, 83.  
 Eutropic series, 267.  
 Expansion, coefficient of, 27.  
 Fats, analysis of, 203.  
 Fenchone, constitution of, 101.  
 Fermentation, alcoholic, 88.  
 Ferrocyanides, analysis of, 201.  
 Ferrous salts, estimation of, 189.  
 Fertilisers, action of, 255.  
 Flavanthren, 153.  
 Flavone group, the, 149.  
 Fluorescence, relation of, and colour, 130.  
 Fluorine, determination of, 186.  
 Freezing point, depression of, 19.  
 Friedel and Crafts' reaction, 80.  
 Gas analysis, 196.  
 apparatus for, 196.  
 Glucose, constitution of, 87.  
 Glycogen, 224.  
 Gold, colloidal, 58.  
 detection of, 184.  
 Graphite, colloidal, 57.  
 Grignard reaction, 77.  
 Growth of plants, chemical changes during, 252.  
 Guanylic acid, 219.

- Hæmatem, constitution of, 153.  
 Hæmatoxylin, constitution of, 150.  
   use of, as indicator, 185.  
 Hæmatoxylinic acid, constitution of, 152.  
 Halogens, separation of, 185.  
 Helium, detection of, 182.  
   liquefaction of, 60.  
 Heterocyclic systems, 84.  
 Holoquinoids, 124.  
 Homocyclic systems, 84.  
 Hydrazine, formation and oxidation of, 66.  
 Hydrazones, 140.  
 Hydrindones, synthesis of, 117.  
 Hydrocarbons, absorption spectra of, 131.  
   behaviour of, at high temperatures, 84.  
   coloured, preparation of, 129.  
   cyclic, reactions of, 111.  
 Hydrogen, atomic weight of, 36.  
   preparation of, 62.  
   peroxide, detection of, in air, 196.  
   formation and decomposition of, 48.  
   persulphides, 53.  
 Hydrogenation, 75.  
 Hydrolysis, measurement of, 23.  
 Hydroxyazo-compounds, 140.  
   constitution of salts of, 146.  
 Hydroxylates, 67.  
 Hydroxylamine, 66.  
 Hydroxylic compounds, formation of, 113.  
 Hypochlorites, detection of, 186.  
  
 Iminazoles, synthesis of, 117.  
 Imino-esters, hydrolysis of, 83.  
 Indazoles, synthesis of, 116.  
 Indicators, theory of, 184.  
 Indigoid dyes, 156.  
 Indigotin, 156.  
   separation of iron from, 190.  
 Indium selenate, 64.  
 Indole, detection of, in pus, 209.  
 Inorganic substances, indexing of, 33.  
 Iodates, estimation of, 186.  
 Iridium, complex salts of, 54.  
   oxides of, 72.  
   use of, for crucibles, 195.  
 Iron, complex salts of, 56.  
   detection of, in presence of copper, 190.  
   estimation of, 190.  
   rusting of, 71.  
 Isomeric change, 89.  
 Isomorphism, 268.  
  
 Jateorrhizine, 169.  
 Jecorin, 241.  
 Kephalin, 239.  
  
 Kerasin, 235.  
 Ketens, 84.  
   classification of, 85.  
 Ketones, amino-, preparation of, 114.  
    $\beta$ -Ketonic esters, synthesis of, 79.  
  
 Lead, atomic weight of, 38.  
   estimation of, 188.  
 Lecithin, 236.  
 Lipoids, 229.  
 Liquids, crystalline, 103.  
 Lithium, separation of, from other alkali metals, 192.  
 Lymphocytes, 222.  
  
 Magnesium, colloidal salts of, 59.  
 Malt analysis, 207.  
   soluble nitrogen compounds in, 253.  
 Manganese, detection of, 183.  
   estimation of, 192.  
 Manures, 255.  
 Mass, conservation of, 3.  
 Mercuric chloride, detection of, in nitro-cellulose, 183.  
 Mercury, complex salts of, 57.  
   estimation of, 188.  
   vapour, detection of, in air, 196.  
 Merquinoids, 124.  
 Mesotropy, 90.  
 Metabolism, 220.  
 Metals, catalytic action of, 74.  
   preparation of colloidal, 58.  
   rapid electrolytic separation of, 194.  
 Metanil-yellow, use of, as indicator, 185.  
 Metastable state, 26.  
 Methane, synthesis of, 84.  
 Methyl alcohol, detection of, in ethyl alcohol, 198.  
 $\alpha$ -Methylcamphor, 102.  
 2-Methylcarvenene, 100.  
 Methyllethylaniline oxide, resolution of, 108.  
 Methylsparteine, 169.  
 Migration, 92.  
 Milk, analysis of, 208.  
 Molecular constitution, 38.  
   volume, 28.  
   weight, 28.  
 Molybdenite, new element from, 35.  
 Molybdenum, complex salts of, 56.  
 Morpholquinone, synthesis of, 168.  
  
 Naphtho-blue, 164.  
 Neodymium, detection of, 184.  
 Nickel, detection of, 182.  
   estimation of, 190, 194.  
 Nipponium, 35.  
 Nitric acid from the atmosphere, 67.  
 Nitrides, 65.  
 Nitrification, 244.

- Nitrites, production of, from atmospheric nitrogen, 67.  
 Nitro-compounds, aromatic, reduction of, 112.  
 Nitrogen, determination of, in soils, 257.  
     fixation of, 242,  
     peroxide, detection of, in air, 196.  
 Nucleic acid, 218.  
 Nutrition, chemistry of animal, 255.  
  
 Oils, analysis of, 203.  
 Optical activity, 105.  
 Origanene, 100.  
 Osmotic pressure, 13.  
 Oxazines, 160.  
 Oxidation of aromatic substances, 111.  
 Oxides, reduction of, 43.  
 Oximes, formation of, 83.  
 Oxonium salts, 154, 156.  
 Ozone, detection of, in air, 196.  
     formation of, 49.  
 Ozonides, 93.  
  
 Palladium, atomic weight of, 38.  
     colloidal, 58.  
     hydrated sesquioxide of, 46.  
 Palmatine, 170.  
 Paraffins, molecular volumes of normal, 273.  
 Perchlorates, crystalline structure of, 264.  
 Periodates, estimation of, 186.  
 Permanganates, crystalline structure of, 264.  
 Peroxides, 47.  
 Per-salts, 47.  
 Perstannates, 51.  
 Persulphates, formation and reactions of, 51.  
 $\alpha$ -Phellandrene, synthesis of, 100.  
 Phenolphthalein, 184.  
 Phenols, chlorination and bromination of, 128.  
 Phenophenanthracridine, synthesis of, 120.  
 Phosphates, detection of, in minerals, 184.  
 Phosphatides, 230, 235.  
 Phosphoric acid, estimation of, 187.  
 Phosphorus, estimation of, 187, 196.  
     forms of, 40.  
     and its compounds, glowing of, 67.  
     sulphides, 68.  
 Photochemical reactions, 12.  
 Photochemistry, 11.  
 Phrenosin, 235.  
 Physical properties, relations between, 26.  
 Picric acid, estimation of, 201.  
 Plasteins, 217.  
  
 Platinum, detection of, 181.  
 Polyhalides, 54.  
 Polypeptides, 170.  
 Potassium, precipitation of, as cobalt-nitrite, 192.  
     nitrate, crystalline form of, 277.  
 Praseodymium, detection of, 184.  
 Propiolic acid, synthesis of, 79.  
 Protagon, 231.  
 Protein nomenclature, 212.  
 Proteins, reactions of, 205.  
 Protons, 1.  
 Pruneanilide, constitution of, 160.  
 Pyranol salts, 151.  
  
 Quinones, 122.  
     synthesis of, 123.  
  
 Racemates, triboluminescence of, 13.  
 Radium, atomic weight of, 64.  
     preparation of, from pitchblende, 64.  
 Rare earths, 60.  
 Reactions, mechanism of, 74.  
 Red lead, assay of, 188.  
 Reduction of aromatic nitro-compounds, 112.  
     of oxides, 43.  
 Refractometer, use of, 206.  
 Remite, new element from, 35.  
 Renna, 215.  
 Resorubin, 185.  
 Respiration, 221.  
 Rhodium, complex salts of, 55.  
     use of, for crucibles, 195.  
 Ring formation, 114.  
     synthesis of a seven-membered, 126.  
 Rings, formation of five-membered, 117.  
     heterocyclic, containing oxygen, 147.  
 Rongalite, constitution of, 178.  
 Rosamine, 164.  
 Rosaniline group, the, 164.  
 isorosanindone, constitution of, 162.  
 Rosocyanin, 185.  
 Rotatory power, effect of electrolytes and non-electrolytes on, 24.  
 Ruthenium, detection of, 182.  
  
 Salts, colour of, in solution, 9.  
     complex, 54.  
 Santene, constitution of, 101.  
 Secretin, 238.  
 Selenates, crystalline form of alkali, 265.  
 Selenium compounds, organic, 179.  
 Selenonium derivatives, 179.  
 Sensitisers, theory of, 12.  
 Sewage, analysis of, 197.  
 Silica as catalyst, 77.  
     estimation of, in acetylene, 196.  
 Silicon compounds, organic, 175.



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